

HSA/DOSE RECONSTRUCTION

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3/15/95

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ORNL
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RALA - CHEMISTRY DEVELOPMENT (1948 *)

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David R. Hamlin 3/9/95
Technical Information Officer Date
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49-4-209 Report on Los Alamos RaLa Meeting, April 13 and 14, 1949.

50-2-3 RaLa Design File.

FLS-162 Purification of Ba¹⁴⁰ by Ion Exchange.

The Extraction, Concentration, and Decontamination of Ba¹⁴⁰ from Uranyl Nitrate Decontamination of Ba¹⁴⁰ from Uranyl Nitrate Solutions by an Adsorption Process.

Purification of Ba¹⁴⁰ by Ion Exchange. Period 2/10/49 - 3/10/49.

Purification of Ba¹⁴⁰ by Ion Exchange. Period Ending 3/10/49.

Purification of Ba¹⁴⁰ by Ion Exchange. Period 2/10/49 - 5/10/49.

Dwg. 7191 Copy 1A

Dwg. 7192 Copy 3A

Barium 140 Separation Development in the Semi-Works. Date 5/4/49.

FLS-80 Purification of Ba¹⁴⁰ by Ion Exchange. Period 5/10/49 - 6/10/49.

FLS-98 Purification of Ba¹⁴⁰ by Ion Exchange. Period 6/10/49 - 7/10/49.

Dwg. 7317 Copy 1A

FLS-116 Purification of Ba¹⁴⁰ by Ion Exchange. Period 5/10/49 - 8/10/49.

Dwg. 7534 Copy 1A

Dwg. 7535 Copy 1A

FLS-133 Purification of Ba¹⁴⁰ by Ion Exchange. Period 8/10/49 - 9/10/49.

FLS-181 Purification of Ba¹⁴⁰ by Ion Exchange. Quarter Ending 11/10/49.

FLS-202 Purification of Ba¹⁴⁰ by Ion Exchange. Date 12/10/49.

FLS-225 Purification of Ba¹⁴⁰ by Ion Exchange. Period 12/10/49 - 1/10/50.

FLS-244 Purification of Ba¹⁴⁰ by Ion Exchange. Month Ending 2/10/50.

FLS-272 Purification of Ba¹⁴⁰ by Ion Exchange. Month Ending 3/10/50.

FLS-296 Purification of Ba¹⁴⁰ by Ion Exchange. Month Ending 4/10/50.

FLS-332 Purification of Ba¹⁴⁰ by Ion Exchange. Quarterly Report.

FLS-374 Purification of Ba¹⁴⁰ by Ion Exchange. Month Ending 6/10/50.

FLS-422 Purification of Ba¹⁴⁰ by Ion Exchange. Period 5/10/50 - 8/10/50.

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2.

OAK RIDGE NATIONAL LABORATORY

April 19, 1949

TO: Mr. C. N. Rucker

FROM: Mr. L. B. Emlet

SUBJECT: Report on Los Alamos RaLa Meeting, April 13 and 14, 1949

A series of three meetings were held on Wednesday and Thursday, April 13 and 14, 1949, at Los Alamos to discuss the future of the RaLa program. The various installations were represented by the following persons:

Hanford Engineer Works - C. N. Gross, H. M. Parker, W. M. Harty, B. Widenbaum,
L. Staepler, R. Smitser, John Carleton.

Hanford AEC - Don Sturgess.

Los Alamos Laboratory - John Manley, E. Jette, Don Mueller, R. P. Hammond,
J. A. Leary, D. P. McDougal, N. H. Smith, J. R.
Lilienthal.

Washington AEC - A. V. Peterson.

Oak Ridge AEC - H. M. Roth.

Oak Ridge Nat'l Lab. - F. L. Culler, Jr., L. B. Emlet.

The following items were discussed:

I. OVERALL RALA REQUIREMENTS

The following RaLa requirements were set up by A. V. Peterson and agreed to by the Los Alamos people:

1. 4/25/49 to 6/30/49

Four - 2500-curie shipments at three-week intervals.

2. 7/1/49 to 6/30/50

Ten - 2500-curie shipments. It is possible that in some cases two of these shipments will need be combined to supply a 5000-curie source.

3. 7/1/50 for indefinite period

Eight - 10,000-curie shipments.

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II. STATUS OF RALA PROGRAM AT HANFORD, LOS ALAMOS, AND ORNL

1. Messrs. Gross and Harty reviewed the present status of the RaLa program at Hanford. The following points were mentioned:

- a. Hanford completed a feasibility report early in January on the construction of a new RaLa production unit. They estimated a total cost of \$4,000,000 to install a plant based on the present ORNL process. They believe that this plant can be in operation by July, 1950, if the project is given sufficient priority.
- b. The AEC in a letter to General Electric expressed the opinion that \$4,000,000 was too high and suggested that consideration be given to using the two pilot plant cells in the end of the "T" Canyon for a RaLa production facility. They further pointed out that only \$750,000 had been budgeted for RaLa production during 1950 and suggested that the development and construction program be held within this limit.
- c. Hanford is at present studying the feasibility of using the "T" Canyon and they expect to have a report, including estimated costs, time schedule, etc., completed by late June, 1949.
- d. Hanford is basing their process on the current obsolete ORNL procedure. They plan to use a 26" centrifuge for the initial Ba-Pb sulphate separation. All equipment will be designed for remote control maintenance. A minimum of development work is planned in an attempt to increase the purity and the yield of the process.
- e. Mr. Gross stated that, although the report is not complete on the use of the existing cells in the "T" Canyon, they were of the opinion that neither the time schedule nor the money limitation would be met if the acid purification step (fuming HNO_3 and ether-HCl steps in the glassware) were included in the Hanford operation. He suggested that this step be combined with the Los Alamos Ia^{140} separation step.

2. Mr. Hammond and later Dr. Jette reviewed the status of the RaLa program at Los Alamos.

- a. A new Ia^{140} separation unit is being constructed at Los Alamos. It should be completed and ready for operation some time after February, 1950. At that time they will want to gradually increase the size of the batches processed from 2,500 to 10,000 curies. They expect the new

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2. a. Continued

equipment to be more tolerant of inactive contaminants (Fe, Ni, Cr, Pb, etc.).

b. The greatest difficulty in present RaLa shipments appears to be the organic and metallic contaminants. The last shipment (Run 31) did not show any evidence of the organic contaminants but there were relatively large amounts of iron present. It is believed that if a NaOH purification step is incorporated with the present acid purification that most of the interfering contaminants will be removed.

c. Mr. Hammond and Dr. Jette stated that they did not believe it possible to transfer the acid purification step to Los Alamos without drastically changing the design of their new facilities and adding a liquid waste disposal problem.

3. Messrs. F. L. Culler, Jr., and L. B. Emlet reviewed the RaLa program at ORNL using the recent report as a guide (CF #49-4-38; RaLa Process Study - Preliminary Report No. 1; F. L. Culler, et als, to L. B. Emlet; 4/6/49).

a. The RaLa production unit is one of the major contributors to the Laboratory particle problem and, therefore, immediate process modifications are required. It is also planned to alter the Ba-Pb sulfate separation step and attempt to develop an improved purification method to insure a better quality product. A cost of \$127,000 (exclusive of overhead) is estimated for these modifications. These changes do not provide for increased batch sizes, but will make the production of 2500-curie batches more reliable. The Laboratory management is of the opinion that this work must proceed at once so long as ORNL is expected to continue producing 2500-curie batches.

b. It was proposed that the AEC approve a more drastic modification of the ORNL RaLa facilities to provide for 10,000-curie batches. This would entail eight to fourteen months elapsed time and an expenditure of \$394,000 (exclusive of overhead).

c. In conjunction with the above it was suggested that work start immediately on the development of a new process. This new process should be aimed at providing the design of a permanent Ba¹⁴⁰ separation unit at the site of the Hi-flux reactor or at Hanford.

d. The ORNL group further suggested that RaLa construction work at Hanford be curtailed until a better process, expected to result from the proposed development work, was available.

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III. PRODUCT SPECIFICATIONS

Mr. Hammond of Los Alamos admitted that although product specifications had been written, very few, if any, shipments had ever been within these specifications yet some of the shipments had yielded a satisfactory La^{140} source. In short, the existing specifications do not mean anything. Accurate specifications and a method of determining the contaminants is a phase of the development work. Los Alamos agreed that their new processing equipment could stand a scale up of inactive contaminants with an increase in the Ba^{140} batch size. It was suggested that until better specifications are available that the following be used where possible:

	<u>2200-curie Batch</u>	<u>10,000-curie Batch</u>
Inactive Lead.....	Less than 50 mg.....	Less than 225 mg.
Inactive Iron.....	Less than 10 mg.....	Less than 45 mg.
Inactive Chromium.....	Less than 5 mg.....	Less than 25 mg.
Inactive Strontium.....	Less than 50 mg.....	Less than 225 mg.
Inactive Nickel.....	Less than 5 mg.....	Less than 25 mg.
Inactive Barium.....	Less than 1300 mg.....	Less than 6 gm.

Mr. Mueller listed the quantity of radioactive contaminants that could be tolerated in the completed La^{140} source. This La^{140} source is supplied by the Los Alamos process; therefore, the quantity of contaminants in the material as it leaves Oak Ridge (or Hanford) can be considerably greater than those listed below. Los Alamos will supply the maximum radioactive contaminants for the Ba^{140} product.

: 10,000 to

$T_{\frac{1}{2}}$ - Radioactive Contaminants: 0-10d : 10-100d: 100-1,000d: 1000-10,000d: 100,000d
 Curies of Contaminants : 100 C.: 0.01 : 0.001 : 0.0001 : <0.0001

Ce / Pr - $T_{\frac{1}{2}}$ = 1/5 of above
 Ru / Rh - $T_{\frac{1}{2}}$ = 1/5 of above
 Sr - Y - $T_{\frac{1}{2}}$ = 1/30 of above
 Pu - 4/10,000 of above.

The above figures were arrived at by calculation assuming each test site is used every six weeks and that only 1/6 of the above contaminants are deposited in the testing area.

IV. RESULTS OF MEETING

1. A. V. Peterson requested that ORNL submit to the Oak Ridge AEC as soon as possible (tentatively by 4/25/49) a detailed proposal for modifying the existing equipment to produce 10,000-curie batches. This proposal should indicate what portion of the total cost is included in the present Laboratory budget and how much additional money will be required.
2. This same letter to the AEC, if possible, should include the ORNL proposal for a development program on a new process. Time schedules, interfering programs, manpower requirements, etc., should be mentioned.

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3. Hanford was requested to study the feasibility of exposing U^{235} foil in the "W" piles.
4. Los Alamos was requested to investigate the separation of Ba^{140} from irradiated U^{235} foil and the decontamination of the U^{235} for recovery. (A decontamination factor of 10^9 to 10^{10} was believed to be necessary.)
5. ORNL agreed to study the inert and radioactive contaminants of the present product.

L. B. Emlet
L. B. Emlet

LBE:wp

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WKE
8

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Date: 2-1-50
To: RaLa Design File
From: F. L. Culler
Subject: Conference on RaLa Progress

This document consists of 2
pages. No. 5 of 11 copies.
Series A.

SAFETY NATIONAL LABORATORY
CENTRAL FILES NUMBER
50-2-3

Before reading this document sign and date below:

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|---|--------------------|
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| 2. J. A. Swartout | 8. L. B. Emlet |
| 3. J. O. Davis | 9. E. J. Witkowski |
| 4. F. R. Bruce | 10. R. E. Blanco |
| 5. W. K. Eister  | 11. I. R. Higgins |
| 6. W. E. Unger | |

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To: RaLa Design File

From: F. L. Culler

Subject: Conference On RaLa Progress

February 1, 1950

Present: Steahly, Swartout, Davis, Bruce, Eister, Unger, Culler, Emlet, Witkowski.

A meeting to discuss the results of the recent high level RaLa resin column run and to discuss future program was held on January 27, 1950. The following summarizes important points of the discussion:

1. Members of the Chemical Development Section expressed confidence in the resin column process for barium purification as a result of the two high level runs just concluded. Resin stability has been demonstrated at high level of radiation and the general operability of the acid-citrate and the one column Versene process. No additional runs will be required in the resin cubicle unless data collected during the high level runs reveal previously unknown problems. If this is the case, another run should be made with regular RaLa production material at as high an activity level as possible. Los Alamos, of course, must agree to this test.
2. Unger, Higgins, and Blanco will concentrate on the preparation of a report for RaLa in the coming two weeks. In addition to a major report, a supplementary letter to be transmitted to the AEC outlining results of RaLa process development and the construction program at ORNL.
3. Emlet said that at the present time no definite schedule had been established for Bldg. 706-D alterations. However, an attempt will be made to finish the design so that construction may start some time around June 1, 1950.
4. A construction request is necessary to provide money for the design of the RaLa facilities. The development budget for fiscal year 1949 has already been overrun. Emlet indicated that the Atomic Energy Commission is waiting for the construction request.
5. Plant design will proceed on the basis of the installation of a crud filter, of a process filter, the one column Versene process in which metathesis is still necessary. Handling and loading facilities for the new Los Alamos carrier will be designed and installed. Design work will now proceed with the utmost haste with less attention being given to assistance in the development program.

Floyd L. Culler

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48-10-396

10

FLS-162
Technical Division
Chemical Technology
Department

To: F. L. Steahly

Date: October 7, 1948

From: R. E. Blanco

Report Period: Month ending

Distribution:

This document consists of Oct. 7, 1948 6
pages and 0 figures.
1 of 6 Series MC

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Problem No. TDSI-30

Part

M O N T H L Y R E P O R T

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey

Secret Notebook No.

SUMMARY

The Acetate-Citrate Process for recovery and purification of Ba¹⁴⁰ by ion exchange is being pilot planted in the semi-works at present. Development work is under way to improve this process by the use the aqueous soluble chelation agent "Versene" (ethylene diamine tetra acetic acid) instead of the acetate. The Versene Acetate process would proceed as follows:

- (1) Dissolve the barium - lead sulfate in versene and adjust the pH to 6.5 to 7.0. This reaction proceeds very easily and is quantitative.
- (2) Pass onto Dowex 50 resin column where barium is adsorbed while the bulk of the cations and all of the sulfate pass through.
- (3) Selectively elute remainder of cationic impurities and elute barium in 6 M nitric acid as in the present process.

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AEC 4-19-61

M. Shirley
For: M. T. Gray, Supervisor
Laboratory Records Dept.

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Consideration of the equilibrium data shows that the strength of the "Versene" complexes decrease with pH and that in the range pH 6.5-7.0 the percent barium complexed is low while the strontium and especially the lead are still complexed to a higher degree. Empirical experiments show that ^{7.1}~~9.5~~ $\times 10^{-3}$ moles of "Versene" is the minimum amount necessary to dissolve 1 gm of lead and 10 mg of barium as the sulfates, and 10 mg each of iron, nickel, and chromium (1/100 RaLa scale) at a pH of 6.5 in 60 ml of solution.

Under these conditions up to 60% of the barium can be adsorbed on 20 ml of Dowex 50 resin. IRC-50 resin was found to be no better. By increasing the amount of resin it is expected that all the barium can be adsorbed.

Two procedures are being considered for the separation of barium from the uranium dissolver solution to replace the lead sulfate precipitation. The uranium can be complexed at pH 6.0-7.0 with "Versene" so that it may be possible to separate the barium from the uranium by ion exchange using IRC-50 resin thus making use of the preferential selectivity of this resin for the alkaline earths. A ~~more~~ ^{preferable} preferential complexing agent might be bi-carbonate at higher pH's as the capacity and selectivity of IRC 50 for alkaline earths has been shown to increase with pH. ~~However~~ Consideration of the equilibria show that the Ks.p of barium carbonate may not be exceeded under these conditions, ^{however,} its exact solubility will be determined. "Versene" might possibly be used to complex and dissolve the uranium in the Hanford waste tanks at a pH of approximately 7. The "Versene" could easily recovered for recycle by acidifying and filtering off the precipitated "Versene".

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Discussion:

I. Investigation of Versene in the RaLa Process

A. Dissolution of Barium and Lead Sulfate

"Versene" (ethylene diamine tetra acetic acid) is a strong complexing (chelation) agent. The complexes are so strong that such compounds as barium and lead sulfate are easily dissolved. Consideration of the equilibria in this system by means of the equilibrium constants listed by Schwarzenbach in *Helv. Chimica Acta* 30, 1798 (1947) and 21, 1029, (1948) leads to the following equation:

$$\frac{[H]^2 [Ba Y^{-2}]}{[Ba^{+2}] [H_2 Y^{-2}]} = K_{ack1}, K_{ack2}$$

where Y^{-2} is the versene anion. Thus the amount of free Ba can be calculated for any pH and versene concentration. It is found that at a pH of 6.5 to 7, the % Ba complexed is low while the Sr and especially the Pb are still in the complex form. If the equilibrium constants for Pb were known it would be possible to calculate the minimum amount of Versene needed to dissolve barium and lead sulfate at pH 6.5 from the fact that the amount of free barium should not exceed the Ks.p of $BaSO_4$.

Empirical experiments in the laboratory have shown that ^{7.1}~~9.5~~ to ^{7.9} 10.6×10^{-3} moles of Versene is the minimum amount necessary to dissolve 1 gm lead and 10 mg barium as the sulfates, and 10 mg each of iron, chromium, nickel (1/100 RaLa scale) at a pH of 6.5 in 50-60 ml of solution.

Feeds of this composition at pH's of 6.5 and 7.0 have been passed through 10 and 20 ml of Dowex 50 resin (sodium form) and 10 ml of IRC 50 resin (sodium form, buffered to pH 6.8 with sodium acetate). Under these conditions it has been found that up to 60% of the barium is adsorbed on the resin while all the sulfate and the bulk of the other cations pass through the column. Larger amounts of resin will be tried in order to increase the barium yield. (See Table 1).

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The small amount of cations adsorbed with the barium can be selectively eluted as in the acetate-citrate process to obtain pure barium.

B. Uranium Complexing Agent

It has been found that the mole ratio of $\frac{UO_2^{++}}{\text{"Versene"}} = \text{approx. } 1$ in the soluble complex at a pH of 7.0 and that the molarity of UO_2^{++} can be at least as high as 0.27. This ratio decreases with pH. In the RaLa process it may prove advantageous to complex the uranium in the dissolver solution with Versene at a pH of 6.0 to 6.5 (where the barium is not complexed) and pass through an IRC 50 or Dowex 50 resin column. Recent determinations of barium distribution coefficients have shown that at pH 6.0 the K exchange for Ba is no higher for IRC-50 than for Dowex 50.

II. Dissolution of Uranium in Hanford Waste By Versene at High pH.

A scouting experiment showed that Versene might possibly be used to complex and dissolve the uranium in the Hanford waste tanks at a pH of 6-7. Three 10 ml sample of synthetic Hanford waste (slurry + supernate) were diluted to approx. 500 ml, made 0.06M in versene, and adjusted to pH's 6.0, 6.8, and 11. The percent of U in solution was approx. 10% at pH 11 and the order of 50-90% in the range 6.0-6.8. At pH 5 in 0.12M versene the % uranium in solution was close to 100%. It was not determined whether the large delution (50X) was necessary.

The versene could be easily recovered for recycle by acidifying and filtering out the precipitated "Versenic" acid at pH 1.0. Versene costs about 0.60/lb. The above figures are only semi-qualitative as the accuracy in sampling the slurry feed is low.

III. Equilibrium Considerations in Using Bi Carbonate-Carbonate As a Complexing Agent for Uranium in the RaLa Process

Determination of barium distribution coefficients using IRC-50 have shown that the barium distribution coefficient increases with pH and is approx. 35 times

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higher at pH 9.0 than at pH 6.0. This is probably due to the formation of a ring structure in the resin with di-valent cations at the higher pH. This point will be discussed more fully next month when the complete distribution results will be reported. It is evident that using bi-carbonate to complex the uranium at a pH of 7.5 will make use of the most favorable barium distribution coefficients. Bersohn and Brady in MonC-109 report that a 0.4M bi-carbonate solution will complex uranium to the extent of 0.2 mole/liter i.e. 0.2M at pH 7.4. The molarity of barium in dissolver solution of this concentration is 2.53×10^{-5} M. Barium bi carbonate is soluble but the K_{sp} of $BaCO_3$ is 8.1×10^{-9} in H_2O . Therefore the $CO_3^{=}$ in equilibrium with 0.4 M bi carbonate at pH 7.8 must be determined to see if the barium will remain in solution. The equilibrium concentration of carbonate under these conditions was calculated to be 4.51×10^{-4} M while the maximum acceptable concentration calculated from the K_{sp} would be 3.2×10^{-4} . However, in the uranyl solution the solubility of barium carbonate would be expected to be somewhat higher. The solubility of barium carbonate under these conditions will be determined by radio chemical technique.

Table 1

Recovery of Ba¹⁴⁰ By Ion Exchange From A Solution of Ba and P₂SO₄ In

Versene

Conditions:

Column: Runs 2-6: 10 ml Dowex - 50 Resin, 100-200 mesh
" 8-10: 20 ml " " "

Run 9: 5 ml (Air dry, H⁺-form) IRC-"50" resin, 60-80 mesh

Activation: For all runs except Run 9: Resin initially converted to Na⁺-form with conc. NaNO₃ and H₂O washed.

Run 9: Resin initially converted to Na⁺-form with 1.0M NaOH(up-flow), and buffered (down-flow) with 1.0M Na-acetate, pH 6.8.

Feed: 10 mg, each, of Ba, Cr, Ni and Fe; 1 gm. Pb; 1 mg Sr + 10 ml Ba "tracer"

Volume: 50-60 ml.

Flowrate: 0.55 ml/cm²/min.

Run No.	Feed pH	Moles Versene Present in Feed	Ba Yield %	Ba Material Balance (%)
2	7.0	.0106 .0079	29.28	76.28
3	6.5	"	60.27	88.66
4	6.0	"	(disregarded-feed cloudy)	
5	7.12	.0054 .0071	11.7	101.08
6	6.5	.01007 .0075	35.0	70.8
8	7.0	.0105 .0079	22.65	86.01
9	6.5	.01007 .0075	16.2	78.2
10	6.5	" "	56	100

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Drawing # 7536

RESTRICTED DATA

100 gms Pb as PbSO₄
1 gm Ba as BaSO₄
Impurities:
Fe, Ni, Cr, and Sr

PROCESS I:
Dissolve in 6 N NaOH (CO₃ - Free); Dilute to 0.6 N NaOH
Volume = 20 Liters

PROCESS Ia:
Make 0.5 M in NaOH (CO₃ - Free)
Volume = 20 Liters

METATHESIS PRODUCT:
Pb+2
Ba+2
In dilute HNO₃

PROCESS II:
Dissolve in 1.0 M Na acetate
Volume = 20 Liters

PROCESS IIa:
Make 0.5 in Na acetate
Volume = 5 Liters

CENTRIFUGE:
Remove Fe, Cr, and Ni As hydrous oxides

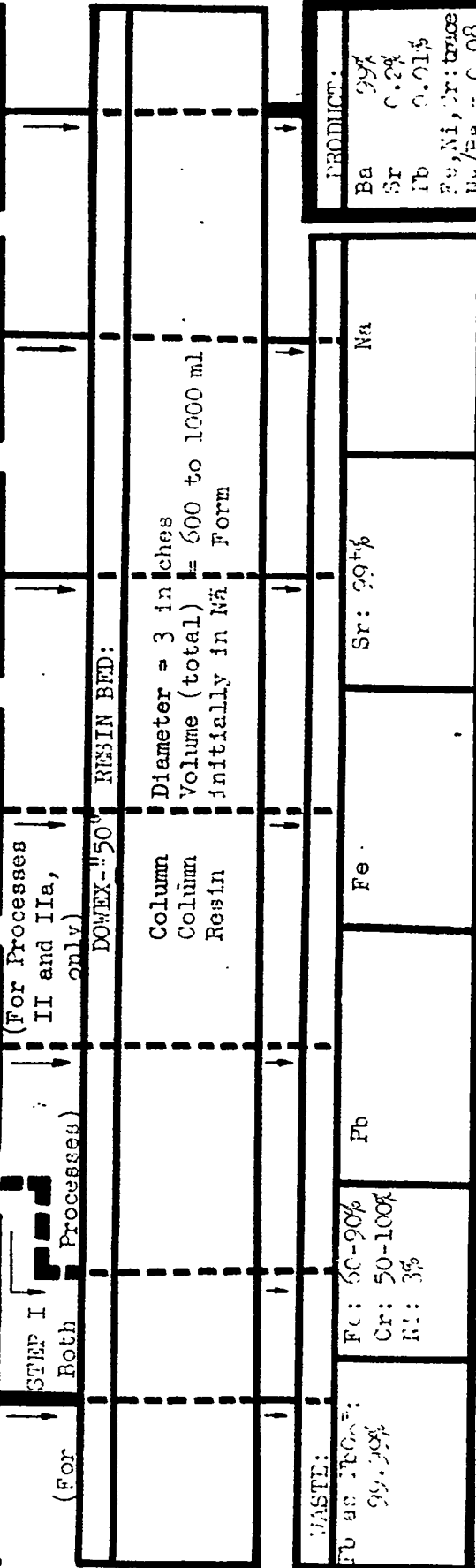
STEP I A
WASH:
0.5 M NaOH (CO₃ - Free)
Vol. = 5 Liters

STEP I B
WASH:
0.5MNa citrate pH 3
Vol=8-10 Liters

STEP II
WASH:
0.1MNa citrate pH 9
Vol=6-10 Liters

STEP II I
WASH:
6 N HCl
Ca. 2 Liters

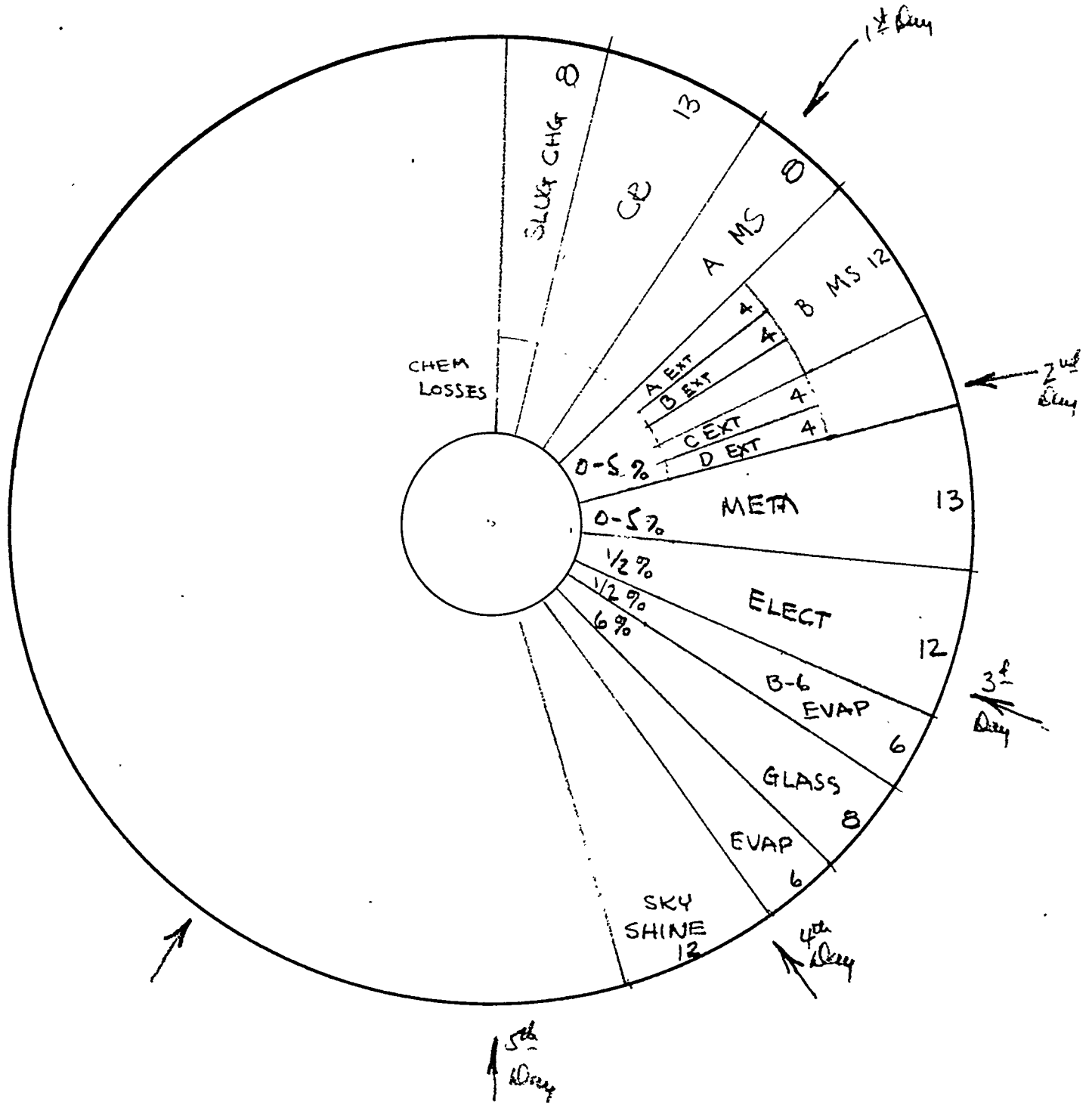
STEP IV
ELUTING AGENT
6 N HNO₃
1.5-2.0 Liters



* Under Na (CO₃ - Free) Atmosphere.

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Drawing # 7009



AT DISCHARGE 9900
 AS RECEIVED 7530
 AFTER PROCESS
 15% CHEM. LOSS
 17% DECAY LOSS 4970

IMP CYCLE (85%)
 76 W SLOGS
 4970 CURIES

CN-2563

The Extraction, Concentration, and Decontamination of Ba^{140} from Uranyl Nitrate
Decontamination of Ba^{140} from Uranyl Nitrate Solutions by an Adsorption Process.

February 1, 1945

Period: Dec. 1, 1944 to Jan. 15, 1945
Report prepared by J. Schubert

An all adsorption process has been developed for the extraction, concentration and decontamination of Ba^{140} from active uranyl nitrate solutions, and its chemical feasibility has been demonstrated on a laboratory scale. In a series of six flow-sheet test experiments consisting of an extraction cycle followed by two concentration decontaminating cycles an average over-all yield for Ba^{140} of 87% was obtained. This recovery was accompanied by a 200 fold total volume reduction and a total gamma decontamination of 200. The basic principles of this separations procedure are shown to be: (a) the selective ion exchange adsorption of barium by one of the new resinous yeolites (amberlite IT-1) followed by (b) the selective desorption and re-adsorption of Ba caused by its complex ion formation in ammonium citrate-citric acid solutions. In general the procedure operates as follows:

1. Adsorption of Ba^{140} on the ion exchange resin from an active 10% UNH solution, allowing the weaker adsorbing uranyl ion to exceed the capacity of the resin.
2. Eluting the uranium adsorbed on the resin with 0.25M H_2SO_4 by sulfate complex formation.
3. Elution of the Barium with 5% citric acid at pH 6.
4. Dilution of the 5% citric acid to 0.5% and adjust pH to 2.5 with Hcl.
Feed to a ten fold smaller resin column than used in step #1 with re-adsorption of the Ba.
5. Add 5% citric acid at pH 3 to complex and desorb the rare earth activities leaving the Ba adsorbed.
6. Desorb the Ba with 5% citric acid at pH 6.
7. Repeat steps 4 and 5 using a ten fold smaller resin column and eluting

the final Ba¹⁴⁰ product with 6N HCl instead of 5% citric acid at pH 6.

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Technical Division
 Chemical Process
 Development Section

To: F. L. Steahly

Date: March 10, 1949

From: R. E. Blanco

Report Period: 2/10/49-3/10/49

Distribution: (1) FLS (2) WKE (3) REB (4) FRB (5) FLS

Problem No. TDSI- 30

Part

MONTHLY REPORTTitle: Purification of Ba¹⁴⁰ by Ion ExchangeWork by: R. E. Blanco, A. H. Kibbey, G. C. BlalockSecret Notebook No. C1-1656SUMMARY

An ion exchange process is being developed for the purification and recovery of Ba¹⁴⁰. This procedure would follow the electrolysis step in the present flowsheet and replace the ether-hydrochloride separation. The advantages of an ion exchange process are (1) ease of remote control, (2) higher yield and purity of product.

A survey of available analyses shows that ^{the} solution after electrolysis can be expected to contain the following maximum amounts of impurities in addition to 1 gm of Ba/2000 curies

Pb - 1000 mg
 Fe - 1000 mg
 Sr - 100 mg
 Cr - 223 mg)
 Ni - 166 mg) Estimated relative to amount of Fe present.

The product specifications as stated in the manual of operations for the maximum amounts of impurities allowed ⁱⁿ 2000 curies are as follows:

Pb - 50 mg
 Fe - 10 mg
 Sr - 50 mg
 Cr - 5 mg
 Ni - 5 mg

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March 10, 1949

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Dowex 50 resin has been chosen because of its high stability. The distribution coefficients, K_d , for these 6 cations have been determined between Dowex 50 and 0.5 M citric acid (ph's 1.7, 3.0, and 7.8), 0.4 M oxalic acid (ph's 0.78, 3.0, and 7.8), and 1.0 M ammonium acetate ph 6.0. Oxalic acid will not be investigated further at present as the solubility of the oxalate complexes (with the exception of Fe and Cr) was found to be too low. The analytical results are not available for the acetate system. However, qualitative column runs show that ammonium acetate is effective for lead elution. The distribution coefficients in the citric acid system in the pH range 3.0 to 7.6 indicate the possibility of selectively eluting the contaminants with a small loss of Ba. The Ba would then be eluted with a small volume of hydrochloric acid.

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~~CONFIDENTIAL~~DiscussionEstimation of Starting Solution

The $\text{Ba}(\text{NO}_3)_2$ solution after electrolysis was analyzed for Fe over a series of 15 runs. The average total amount of iron was 234 mg with one batch containing 360 mg and a second one containing 880 mg. Over a series of 43 samples the average amount of Pb was found to be 189 mg with 8 batches over 400 mg and 1 as high as 1 gm. One gm each of Fe and Pb has been selected as the maximum amounts that will be encountered. A survey of the fate of Sr^{89} in the process is given in MonN-134 (CE-R). This report showed that 10% of the total amount of Sr present at the start was removed by the ether hydrochloride step and that 0.4% remains in the product. Spectrographic analysis of a series of 10 runs showed an average of 1.6 mg of Sr in the product and a maximum of 4 mg. On this basis it is assumed that ca. 100 mg of Sr will be present in the solution after electrolyses. The amounts of Cr and Ni are estimated to be 223 mg and 166 mg based on the amount of Fe present and their ratios in stainless steel.

Investigation of Complexing Agents

The distribution coefficients for these cations were determined by saturating 5 ml of Dowex 50 resin with a cation and shaking this resin for 2 hours with 0.5 M citric and 0.4 M oxalic acids at reagent ph, ph 3, and ph 7.6, and with 1.0 M ammonium acetate at ph 6 (see Table #1). The results show that with the exception of Fe and Cr the oxalate complexes have too low a solubility. As precipitation in a resin column is to be avoided no further investigation of oxalate elution will be made at present.

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In general one can assume that the distribution coefficient, K_d , = No. of columns volumes at which the peak of the cation elution curve appears. Also, for a system in equilibrium, about $1/2$ of the material is removed before the peak in a symmetrical curve. The K_d 's listed in Table #1 for the citric acid systems at pH 3 and 7.6 indicate the possibility of selectively eluting the contaminants with a small loss of Ba. The Ba would then be eluted with a small volume of hydrochloric acid.

The analyses are not available for the ammonium acetate system. However, qualitative results show that Pb is removed by ammonium acetate elution.

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Table #1

Distribution Coefficients of Ba¹⁴⁰ and Contaminants
between Dowex 50 and Possible Eluting Agents

Conditions: 5 ml of resin, previously saturated with a cation, was shaken for 2 hours with 25 ml of eluting agent.

$$K_d = \frac{\text{Distribution Coefficient}}{\text{Coefficient}} = \frac{\text{mg of cation/ml resin}}{\text{mg of cation/ml solution}}$$

ppt. indicates a precipitate formed in the solution

Cation Eluted	Eluting Agent					
	0.5 M Ammonium Citrate ph 7.6	0.5 M Citric Acid ph 1.7	0.4 M Ammonium Oxalate ph 7.8	0.4 M Oxalic Acid ph 0.78	0.5 M Citric Acid ph 3.0	0.4 M Oxalic Held ph 3.0
Ni	7.2×10^{-2}	147	ppt.	ppt.	8.3	ppt.
Sr	ppt.	81.9	ppt.	ppt.	15.7	ppt.
Fe	101	13.1	1.1	2.3×10^{-2}	2.0	2.0×10^{-2}
Cr	0.17	61	3.8	28	10	7.0
Ba	ppt.	263	ppt.	266	24.8	ppt.
Pb	ppt.	Very High	ppt.	ppt.	ppt.	ppt.

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To: F. L. Steahly

Date: April 6, 1949

From: R. E. Blanco

Report Period: Ending March 10, 1949

Distribution:

1. FLS *[Signature]*
2. WKE *[Signature]* Problem No. TDSI-30
3. FRB
4. REB Part
5. JOD
6. FLS M O N T H L Y R E P O R T

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey

Secret Notebook No. CL-1656

SUMMARY

Two processes are under development for the improvement of Ba¹⁴⁰ production by use of an ion exchange procedure.

I Citrate - Acetate Process

This process would follow the present electrolysis and evaporation step replacing the ether hydrochloride extraction and would effect the separation of Pb, Fe and other lesser impurities from the Ba¹⁴⁰. The steps in this process are as follows:

- (1) Take the Ba(NO₃)₂ up in 0.5M citric acid and pass through a Dowex 50 resin column where the cations are adsorbed.
- (2) Elute with 0.5M ammonium citrate, pH 3, to remove Fe
- (3) Elute with ammonium acetate pH 6.0 to remove Pb, Cr, Sr, Ni
- (4) Elute the Ba¹⁴⁰ in a small volume of 6N HCl.

(Summary continued on next page)

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April 6, 1949

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A trial run using this procedure showed Dowex 50 resin to be unsuitable because of its slow diffusion rate. As a result, the elutions to remove impurities were cut short because of time limitations. The results showed a 90% yield of Ba, and removal of the following percentages of impurities: Pb, 16%; Fe 82%; Cr, 77%; Ni 100%. Qualitative runs using IR 105 resin have shown it to have a much faster diffusion rate than Dowex 50. Future runs will be made with IR 105 resin and higher molarity of eluting agents.

II Alkaline Process

This process would replace both the electrolysis and ether extraction steps in the present RaLa process. The present electrolysis procedure while adequate in theory, actually leaves up to 1 gm of Pb with the Ba¹⁴⁰. The steps in the proposed ion exchange process are as follows:

- (1) Add enough 0.5M NaOH to hold the Pb in solution as the plumbate and pass through a Dowex 50 resin column. The Ba is adsorbed on the resin while the plumbate anion passes through the column.
- (2) Remove impurities by citrate and acetate elution as in process I.
- (3) Elute Ba¹⁴⁰ in a small volume of 6N HCl. A tracer run using this procedure on 1/10 the ionic Ba concentration of the present RaLa process has been made. 99.5% of the Pb was separated from the Ba. Ba yield was ca. 67%; Ba material balance 85%. Operating time approximately 6 hrs. Refinement of technique and use of IR 105 resin should improve these figures.

Discussion:

Two processes are under development for the improvement of Ba¹⁴⁰ production by use of ion exchange procedure.

I Citrate - Acetate Process

This process would follow the present electrolysis step replacing the ether-hydrochloride extraction and would effect the separation of Pb, Fe, Cr, Ni, and Sr

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from the Ba^{140} by means of selective elution with citric acid and ammonium acetate. The Ba^{140} would then be eluted in 6N HCl. Distribution coefficients for the 6 cations involved between Dowex 50 resin and citric acid and oxalic acids were listed in the monthly report ending March 10, 1949. The distribution coefficients in the ammonium acetate system are listed in Table I-1. The results indicate that the following process should be practical.

- (1) In the ~~proposed~~ ^{present} process the Ba^{140} - HNO_3 solution is evaporated to dryness. This precipitate would be dissolved in 0.5M citric acid and passed through the resin column where the cations are adsorbed. Ammonium citrate (pH 3) would be desirable for this step but cannot be used as Pb is insoluble at these concentrations at pH's higher than about 1.8. Ammonium acetate (in which all the cations are soluble) could be used but would not be so desirable since in this system the Fe would be held higher on the resin column than the Ba. (note its high D.C. in Table I-1).
- (2) The Fe would be removed by selective elution with 0.5M citric acid, pH 3, and the Pb, Cr, Ni, and Sr ~~and~~ ^{with} 1M ammonium acetate, pH 6. pH 7.6 citric acid cannot be used for the separation as the quantities of Pb, Ba and possibly Sr expected to be present in this system are insoluble at this pH. As a result the citrates of these cations precipitate in the resin column thus reducing the flowrate considerably. During further elution the ppt's redissolve but the channelling noted during redissolution impairs clean separation of cations by selective elution. The oxalates have been found to be very insoluble at all pH's so that oxalate elution has not be considered.
- (3) Ba^{140} is then eluted in a small volume of 6N HCl.

A trial run was made following the above procedure on a 1/10 scale as compared to the 706-D process. The results listed in Table I-2 show that a 90%

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yield of Ba¹⁴⁰ was obtained with inadequate separation of all impurities except Ni. The reason for these poor results is the slow diffusion rate of Dowex 50 resin. If an extremely slow flowrate could be used the resin-liquid would be in equilibrium and the favorable distribution coefficients of this system would be fully utilized. However, to effect this elution in a reasonable time a moderately fast flowrate (1 to 2 cc/cm² min) must be used. The above run was terminated before complete separation of the cations was effected as the run time was already of the order of 60 hrs.

Subsequent qualitative runs with IR-105 have shown that Fe can be removed faster from this resin than from Dowex 50 by a factor of 5 or more with 0.5M citric acid due to its higher diffusion rate. A quantitative run is planned where in IR-105 resin will be used as well as eluting agents of higher molarity. Both changes should result in shorter operating times.

II Alkaline Process

This process would replace both the electrolysis and ether extraction steps in the present procedure by an ion exchange process. The present electrolysis procedure while adequate in theory, actually leaves up to 1 gm of Pb with the Ba¹⁴⁰.

The proposed ion exchange substitute process follows:

- (1) The Ba-Pb solution after the metathesis step would be dissolved in 0.5M NaOH essentially free from $\text{CO}_3^{=}$ under an atmosphere of CO_2 free N_2 . This solution would be passed through an ion exchange column previously activated with 1M NaOH where the Ba, Sr would be adsorbed while the plumbate and chromite anions would pass through.
- (2) Wash the column with a small volume of 0.3M HCl. This would dissolve any BaCO_3 , $\text{Fe}(\text{OH})_3$, or $\text{Ni}(\text{OH})_2$ filtered out on top of the resin and allow their adsorption on the resin. It is thought that the amount of Fe, Cr, and Ni present during operations in the new equipment

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will be small. The use of a centrifuge and precipitate washing will eliminate essentially all stainless steel impurities obtained during dissolving while the metathesis container will be tantalum lined.

- (3) A citrate-acetate selective elution step similar to process I would remove the remaining impurities.
- (4) Elute the Ba^{140} in a small volume of 6N HCl.

A run was made to test this procedure using Dowex 50 resin. The results listed in Table II-1 show a loss of 18% Ba in the alkaline Pb - Ba separation step. The 13% Ba lost during NH_4Ac washing was unnecessary as no Pb was removed so that the Ba yield can be considered to ~~be~~ ^{be} 67%. The Ba material balance was 86%. 99.5% of the Pb was separated from the Ba. Refinements of technique and the use of IR 105 resin will undoubtedly produce better results.

Table I-1

Distribution Coefficients of Fe, Pb, Ba, Sr, Cr, and Ni between Dowex
50 and 1M Ammonium Acetate

$$\text{Distribution Coefficient} = \frac{\text{mg cation/ml wet resin}}{\text{mg cation/ml solution}}$$

5 ml of resin saturated with cation were shaken for 2 hours with 25 ml of elutriant.

<u>Cation</u>	<u>D.C.</u>
Pb	1.3
Ni	2.4
Sr	6.5
Fe	21.2
Cr	0.22
Ba	8.9

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April 6, 1949

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Table I-2

Run #1 - Citrate - Acetate Ion Exchange Process for Purification
of Ba¹⁴⁰

Conditions:

Feed: 1/10 ionic scale of Ba¹⁴⁰ process
- 100 ml 0.5M citric acid containing 100 mg each of Ba, Fe, and Pb
10 mg Sr, 23 mg Cr, 16 mg Ni
Elutriants - 525 ml, pH 3 ammonium citrate, 0.5M
315 ml, pH 6 ammonium acetate, 1.0M
150 ml 6N HCl
Flowrate - Ca. 1 cc/cm²/min
Total time - Ca. 60 hrs.
Column - 105 cm x 6 mm - Dowex 50
60-80 mesh

Procedure*

- (1) Pass feed on column
- (2) Elute with citrate followed by acetate
- (3) Remove Ba¹⁴⁰ with 6N HCl

Results:

Ba yield = 90%
% Pb removed = 16%
% Fe " = 82%
% Cr " = 77%
% Ni " = 100%

- * Elution with citrate and acetate terminated before complete removal of impurities due to long time involved.

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Table II-1

Separation of Ba¹⁴⁰ and Pb by Alkaline Ion Exchange Process

Conditions:

Feed: 1/10 ionic scale of Ba¹⁴⁰ process
500 ml of 0.1M NaOH
containing 10 gms of Pb and 100 mg Ba
plus Ba¹⁴⁰ tracer

Column: 17 cm x 1.5 cm - Dowex 50 resin
60-80 mesh, activated with 0.1M NaOH

Elutriant: 150 ml 6N HCl

Flowrate: 1 cc/cm²/min.

Total Time= Ca. 6 hrs.

Procedure:

- (1) Pass feed through column
- (2) Wash with 1 column volume H₂O followed
by 3 column volumes of 0.3M HNO₃
- (3) Wash with 16 column volumes ammonium acetate
- (4) Elute Ba in 150 ml 6N HCl

Results:

99.5% - Pb removed from Ba.
18% - Ba lost in effluent
actual { 13% -* Ba lost in ammonium acetate
Ba { 54% - Ba recovered in 6N HCl
Yield 85% - Ba material balance

* No Pb found in ammonium acetate wash.

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Technical Division
Chemical Process
Development Section


To: F. L. Steahly

Date: May 10, 1949

From: R. E. Blanco

Report Period: Feb. 10 to May 10, 1949

FKS
Distribution:

1. F. L. Steahly 
2. W. K. Eister Problem No. TDSI-30
3. F. R. Bruce
4. R. E. Blanco Part
5. J. O. Davis
6. F. L. Steahly M O N T H L Y R E P O R T

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey, G. C. Blalock

Secret Notebook No. CL-1656

SUMMARY

An ion exchange process has been developed and a tentative flowsheet is presented for the purification and recovery of Ba¹⁴⁰ subsequent to the metathesis step in the RaLa process. The ion exchange process would replace the electrolysis and ether hydrochloride steps now used. The advantages of an ion exchange process are (1) ease of remote control, (2) higher yield and purity of product. A major disadvantage is gas formation due to ionization of H₂O. Development work is underway to investigate the feasibility of up flow in resin columns to minimize operational troubles caused by gas formation. Peroxide will be added to the solutions to simulate gas formation. Optimum geometry of resin column will also be studied.

The Ba¹⁴⁰ product specifications per 2500 curie batch are as follows:

Pb - 50 mg	Cr - 5 mg
Fe - 10 mg	Ni - 5 mg
Sr - 50 mg	

A survey of available analyses (14 to 38 runs) from the present RaLa

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process shows that the Ba solution after electrolyses can be expected to contain the following maximum amounts of impurities in addition to 1 gm. of Ba/2500 curies.

Pb - 1000 mg	Sr - 100 mg	
Fe - 1000 mg	Cr - 223 mg	Estimated relative
	Ni - 166 mg	to amount of Fe
		present

The large amount of Pb present indicates the inadequacy of the electrolysis procedure.

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Alkali- Citrate Process For Ba Purification in the RaLa process by Ion Exchange

Step (1) After metathesis make the Ba-Pb nitrate solution 0.5M in $\text{CO}_3^{=}$ free NaOH. Filter or centrifuge to remove $\text{Fe}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$, and any dissolver crud. Step (2) pass the filtrate through a Dowex 50 resin column (approx. 1 liter of resin) previously activated with 0.6M NaOH where the Ba and Sr would be adsorbed while the plumbate and chromite anions pass through Step (3) After washing the resin with 0.5M NaOH followed by H_2O , the Sr and any trace of Pb remaining would be selectively eluted with 0.5M sodium citrate, pH 7.8. (4) Elute the Ba in 6N HCL (see flowsheet Fig. I)

Trial runs on 1/100 the scale of the RaLa process for the separation of Pb and Ba by the above alkali process show yields of the order of 99% for Ba which contain less than 0.1% of the Pb. The separation of Ba and Sr is reported in the literature. Runs are in progress which are designed to verify and evaluate this separation under the above process conditions.

An alternate ion exchange process, the Citrate-Acetate Process would start after the electrolyses step. This procedure would be less desirable from both an efficiency and ease of operation standpoints than the alkali-citrate process which eliminates the electrolyses procedure. The relative distribution coefficients for Ba, Pb, Sr, Ni, Cr, and Fe between Dowex 50

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resin and ammonium acetate, pH 6.0; oxalic acid pH's 0.78, 3.0, 7.8; and citric acid at pH's 1.7 3.0, and 7.8 have been determined. A number of scouting runs have been made in order to actually test the relative effectiveness of these eluting agents for removing these cations from Dowex 50 and IR 105 resins. Any appreciable quantities of Pb cause difficulties as a result of its low solubility in citrate solutions between pH's of 1.8 and 9.0.

Citrate - Acetate Process for Purification of Ba¹⁴⁰ in the RaLa process by Ion Exchange

At present the solution is evaporated to dryness after the electrolysis step.

Step (1) Dissolve precipitate in 0.5M ammonium acetate and pass through resin column where all cations are adsorbed.

- (2) Remove most of the lead by selective elution with ammonium acetate.
- (3) Remove Fe, Cr, Ni, Sr and the balance of the Pb by selective elution with ammonium citrate, pH 3.
- (4) Elute Ba in 6N HCL.

A trial run using this procedure was not too successful in that too much citric acid was used resulting in the elution of the Ba with the other ions. The exact elution curves will be determined for this system to remedy this condition.

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Experimental

I Determination of Impurities Present After Electrolysis in ^{the} ~~H-1~~ Ra-La Process

The $\text{Ba}(\text{NO}_3)_2$ solution after electrolysis was analyzed for Fe over a series of 15 runs. The average total amount of iron was 234 mg with one batch containing 360 mg and a second one containing 880 mg. Over a series of 43 samples the average amount of Pb was found to be 189 mg with 8 batches over 400 mg and 1 as high as 1 gm. One gm each of Fe and Pb has been selected as the maximum amounts that will be encountered. A survey of the fate of Sr^{89} in the process is given in MonN-134 (CE-R). This report showed that 10% of the total amount of Sr present at the start was removed by the ether hydrochloric step and that 0.4% remains in the product. Spectrographic analysis of a series of 10 runs showed an average of 1.6 mg of Sr in the product and a maximum of 4 mg. On this basis it is assumed that ca. 100 mg of Sr will be present in the solution after electrolysis. The amounts of Cr and Ni are estimated to be 223 mg and 166 mg based on the amount of Fe present and their ratios in stainless steel.

II Investigation of Complexing Agents

The distribution coefficients for these cations were determined by saturating 5 ml of Dowex 50 resin with a cation and shaking this resin for 2 hours with 0.5 M citric and 0.4M oxalic acids at reagent pH, pH 3, and pH 7.6, and with 1.0 M ammonium acetate at pH 6 (see Table #1). The results show that with the exception of Fe and Cr the oxalate complexes have too low a solubility. As precipitation in a resin column is to be avoided, no further investigation of straight oxalate elution will be made at present.

Mixtures of oxalate and citrate at pH 9.0 and oxalate and acetate at pH 7.0 have been tried in an effort to decrease the Fe distribution coefficient at these high pH's thus allowing the use of single elution agent for Ba^{140} purification. The solubility of Ba and Pb was found to be too low in the acetate oxalate system. Their solubilities in the citrate oxalate system (pH 9.0) are

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higher so that this system will be investigated further. (See table # II for solubilities of Pb and Ba in these system).

III Alkali - Citrate Process for Ba¹⁴⁰ Purification

This process would replace both the electrolysis and ether extraction steps in the present Ra-La process by an ion exchange process. The present electrolysis procedure while adequate in theory actually leaves up to a gram of Pb with the Ba¹⁴⁰. The ion exchange process would leave less than 50 mg of Pb with the Ba and at the same time effect the separation of Sr from the Ba¹⁴⁰.

The proposed ion exchange process follows:

- (1) The Ba-Pb nitrate solution after metathesis would be made 0.5M in NaOH ($\text{CO}_3^{=}$ free) under an atmosphere of N_2 to exclude CO_2 , and filtered or centrifuged to remove $\text{Fe}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$, and any dissolver crud present.
- (2) The filtrate would be passed through a small Dowex 50 resin column previously activated with 0.6M NaOH where the Ba and Sr would be adsorbed while the plumbate and chromite anions would pass through.
- (3) After washing the resin with 0.5M NaOH followed by water the Sr and any traces of Pb remaining would be selectively eluted with 0.5M sodium citrate pH 7.8.
- (4) Elute the Ba in 6N HCl. (See flowsheet Fig. I).

Several runs have been made to test the efficiency of the separation of Pb and Ba by this method using both Dowex 50 and IR 105 resins. The Dowex 50 has proved to be far superior for use in an alkaline system in that it does not decompose or swell and the amount of Pb retained is less than ^{0.1%} 0.1%. IR 100 decomposes (color throw) slightly in 0.5M NaOH, swells about 30%, and retains up to 80% of the Pb. These bad features of IR 105 are all a result of the presence of phenol groups in this resin in addition to the sulfonate groups. Presumably a chelate band is formed between the

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ionized phenol and sulfonate groups to complex and thus hold the Pb. The replusion between the ionized phenol and sulfonate groups causes the swelling of the resin particles.

The results of the alkaline break through runs are shown in Table 3. The Ba yield approximates 99% when using either resin and contain less than ~~0.01%~~ ^{0.00%} of the starting amount of Pb in the Dowex 50 runs. This would amount to less than 100mg of Pb on the full RaLa scale where the specifications allow as much as 50 mg.

Runs are in progress which will provide data on the separation of Sr and Ba in this process by elution with sodium citrate (pH 7.8) in a manner similar to that used by E. R. Tompkins J. A. CS 70. 3520, 1948. Using this information as a guide it will be possible to determine the exact amount of citrate needed to remove Sr and any traces of ~~Pb~~ remaining, and leave the Ba on the resin for removal with 6N HCl. Thus the situation illustrated by Run Ba-6 in table 3 will be avoided where too much citrate was used resulting in the elution of the Ba in the citrate instead of the HCl.

IV Citrate-Acetate Process for Ba¹⁴⁰ Purification

Some work is being carried on to develop an ion exchange process for Ba¹⁴⁰ purification which would follow the present electrolysis step and replace the ether-hydrochloride extraction. The major difficulty encountered in this ion exchange procedure is the large amount of Pb (1 gm, see section I) present due to its limited solubility in the most desirable eluting agent, ~~no~~ citric acid, especially at the low pH's necessary to remove Fe. Thus the Pb citrate will precipitate in the resin column unless the column is made large enough so that the Pb concentration is small. Under these conditions it would be necessary to have a 2nd column for volume reduction. A second alternative is the use of less desirable eluting agent, ammonium acetate, ⁱⁿ which all the ions are very soluble. As a result of these difficulties major effort has been placed on the relatively simple alkali-citrate process (section III) where by the Pb is easily and completely separated from the Ba at the same time

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eliminating the electrolysis step.

A number of scouting runs are listed in tables 4 and 5 showing the relative effectiveness of ammonium acetate and citric acids for removal of Ba, Fe, and Pb from Dowex 50 and IR 105 resins. It is seen that for equal conditions (volumes of elutriants, resin etc.) that the ions are removed more quickly from IR 105 resin as a result of its lower exchange capacity and consequent lower no. of plates and its faster diffusion rate. (See runs IR 3 and Ba2) Fe is not eluted by ammonium acetate at pH 3 or pH 6. 2M NH_4Cl elutes Ba almost as effectively as 2M NH_4Ac showing the Ba acetate complex to be relatively weak (see Runs IR 3 and IR 9). Runs IR 10 and Fig. II illustrate the separation of Pb and Ba obtained by elution with 1M NH_4 acetate i.e. 98% of the Ba contained 22% of the Pb.

Utilizing this data a citrate - acetate process for Ba^{140} purification would proceed as follows:

(1) In the present RaLa process the $\text{Ba}^{140} - \text{HNO}_3$ solution is evaporated to dryness. This precipitate would be dissolved in 0.5M NH_4Ac and passed through a resin column in the ammonium form where the cations are adsorbed. Ammonium citrate (pH 3) would^d be desirable for this step but cannot be used as Pb is insoluble at these concentrations at pH's higher than 1.8 and less than 9.0.

(2) Remove most of the Pb by selective elution with NH_4Ac .

(3) Selectively remove Fe, Cr, Ni, Sr and the balance of the Pb with ammonium citrate, pH 3.

(4) Elute Ba in 6N HCl.

A trial run was made in IR 105 resin following the above procedure on a 1/100 scale as compared to the Ra-La process (See table 6). The results showed that 50% of the Fe came thru in the 0.5 NH_4Ac effluent from step

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1, the 2.0M NH_4Ac wash contained 33% of the Pb, and that too much 1.0M ammonium citrate, pH 3, wash was used, as it contained, in addition to 22% the Fe and 62% of the Pb, 104% of the Ba. (Ba Material balance = 105%) a detailed study of the elution curves of Fe, Pb, Sr, and Ba in ammonium citrate pH 3 will provide the information to obtain the separation of these contaminants from Ba.

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Table #1

Distribution Coefficients of Ba¹⁴⁰ and Contaminants between
Dowex 50 and Possible Eluting Agents

Conditions: 5 ml of resin, previously saturated with a cation, was shaken for 2 hours with 25 ml of eluting agent.

$$K_d = \text{Coefficient} = \frac{\text{mg of cation/ml resin}}{\text{mg of cation/ml solution}}$$

ppt. indicates a precipitate formed in the solution

Cation	Distribution Coefficients						
	Eluting Agent						
	0.5M Ammonium Citrate pH 7.6	0.5M Citric Acid pH 1.7	0.4M Ammonium Oxalate pH 7.8	0.4M Oxalic Acid pH 0.78	0.5 M Citric Acid pH 3.0	0.4 M Oxalic Held pH 3.0	1.0M Ammonium Acetate pH 6.0
Ni	7.2×10^{-2}	147	ppt.	ppt.	8.3	ppt.	2.4
Sr	ppt.	81.9	ppt.	ppt.	15.7	ppt.	6.5
Fe	101	13.1	1.1	2.3×10^{-2}	2.0	2.0×10^{-2}	21.2
Cr	0.17	61	3.8	28	10	7.0	0.22
Ba	ppt.	263.	ppt.	266	24.8	ppt.	8.9
Pb	ppt.	Very High	ppt.	ppt.	ppt.	ppt.	1.3

Conditions: Resin

5 ml
sodium
Resin

Eluting Agent

0.5M NaOH
5 mg/ml Pb as PbO_2
0.05 mg/ml Ba⁺²
Tracer Ba

$$K_d (\text{Ba}) = 265$$

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Table II

Approximate Solubility of Ba and Pb in Citric Acid and in Citrate-
Oxalate and Acetate - Oxalate Systems

<u>System</u>		<u>Solubility in mg/ml</u>	
		Ba	Pb
0.125M sodium citrate	pH 9.0	< 2.0	< 6.0
0.125M sodium oxalate			
0.25M sodium acetate	pH 7.0	< ^{0.27} 0.27	< .6
0.125M sodium oxalate			
0.5M ammonium citrate	pH 3	soluble	< .3
" " "	pH 4	"	< .58
" " "	> pH 9.0	"	soluble

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Table #3

Separation of Ba and Pb by Ion ExchangeConditions:

Column: Runs Ba-3 to 6: Dowex - "50" Resin (140-200 mesh)

Resin volume = 10 ml.

Runs IR-5, 8, and 11: IR-105 Resin (40-60 mesh)

Resin volume = 25 ml.

Activation: Resin initially put in Na^+ form with 0.5M CO_3^- Free NaOH.Flowrate: $0.5 \text{ ml/cm}^2/\text{min}$.Feed: 5 mg/ml . Pb as PbO_2^- + 0.05 mg/ml . Ba + Ba "tracer" 0.5M CO_3^- Free NaOH

Feed volume = 202 ml.

Washes:

I: 30 ml. CO_3^- Free NaOH, followed by $30 \text{ ml H}_2\text{O}$ II: As shown (For removal of Sr and Traces of Pb)Ba Elutriant: $300 \text{ ml. } 6\text{N HCl}$.

Run #	% Ba In Effluent + 1st Wash	2nd Wash Solution	% Ba In 2nd Wash	% Pb In 2nd Wash	% Pb in Ba Product	% Ba In Product	Ba Material Balance
Ba-3	0.07	150 ml. 1.0M Na acetate	<.01	<0.156	<.041	97	97.08
Ba-4	-	150 ml. 0.5M Na Citrate	(combined with Ba Product)	<.082	(2nd Wash and Product combined)		
Ba-5	0.15	150 ml. 0.1M Na Citrate pH9	0.14	<0.15	<0.10	100-0.29= >99.5	-
Ba-6	0.33	150 ml. 0.5M Na Citrate pH 7.8	104.5	<0.10	<0.07	0.1	104.83
IR-5	0.026	-	-	-	60	97	97.03
IR-8	0.24	0.5M HCl 1.0M Citric Acid pH 4	0.83 55.7	<0.05	6.66	3.2	106.23
		2.0M ammon. acetate	46.5	31.0			
	0.24	0.3M HNO_3 1.0M Ammon. acetate	-	-	(+ washes): 79.54	(+ washes): 22.5	23

Table 4

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Investigation of Eluting Agents For Removal Of Pb, Fe and Ba From IR-105 Resin

Conditions: 25 ml. IR-105 Resin (40-60 mesh)
Flowrate = 0.5 ml/cm²/min.

Run No.	Adsorbate	Elutrient	Remarks	% of Total Adsorbate Eluted
IR-1	111.5 mg Pb	345 ml. 2.0M ammon. Acetate	Elutrient effluent sampled as follows: First 76 ml. contained 61.3% of the Pb Next 76 ml. " 13.6% " " " " 75 ml. " 4.7% " " " " 117 ml. " 4.0% " " "	Pb=83.76%
IR-2	100 mg Fe	282 ml. 1.0M Citric Acid, pH 3	Color comparison of samples taken at 1 column vol. intervals, indicated a peak occurred at col. vol.'s 3-8; last 40 ml. was almost colorless.	Fe=81.8%
IR-3	100 mg Ba	256 ml. 2.0M ammon. acetate	Elutrient effluent sampled as follows: First 87 ml. contained 79% of the Ba Next 87 ml. " 13% " " " " 87 ml. " 0.38% " " "	Ba=92.4%
IR-4	100 mg Ba	316 ml. 1.0M Citric Acid-pH3	Elutrient Effluent sampled as follows: First 75 ml. contained 81% of the Ba Next 84 ml. " 80% of the Ba Next 73 ml. " 4% " " " Remainder " None " " "	Ba= Ca. 165% (Poor material balance).
IR-6	100 mg Pb	314 ml. 1.0M Citric Acid-pH3, followed by concentrated ammon. acetate	Pb precipitated in column with the citric acid, however, elutrient effluent was sampled as follows: First 111 ml. contained 23.2% of the Pb Next 70 ml. " 7.0% " " " " 68.8 " 5.8% " " " " 64 ml. " 3.84% " " " The ammon. acetate elutrient effluent contained 14% of the Pb	Pb= 54%
IR-9	100 mg Ba	314 ml. 2.0M ammon. chloride	Elutrient effluent sampled as follows: First 72 ml. contained 29% of the Ba Next 92.5 ml. " 48.6% " " " " 82 ml. " 21% " " " " 68 ml. " < 1% " " "	Ba=Ca. 99.5%
IR-10	100 mg Ba + 713 mg Pb	1.0M ammon. acetate	For elution curve see Fig. II.	Ba=97%, CONTAINED Pb=22%

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Investigation Of Eluting Agents For Removal Of Pb, Fe, and Ba From Dowex - "50" Resin

Conditions: *25 ml. Dowex - "50" Resin (60-80 mesh)
Flowrate = 0.5 ml/cm²/min.

Run #	Adsorbate	Elutrient	Remarks	% Of Total Adsorbate Eluted
Pb-1	Resin saturated with Pb + 100 mg. Ba	302 ml. 0.1M NaOH	Pb precipitated in column and was partially redissolved. Concentrated ammon, acetate was used to remove Ba and balance of Pb.	Ba = 97% Pb = 47%
Pb-3	100 mg Pb 100 mg Pb	315 ml. 2.0M ammon. acetate	Elutrient effluent sampled at 75 ml. intervals First 75 ml. contained 48% of the Pb Remaining 240 ml. " 6% " " "	Pb = 54%
Fe-1	100 mg Fe	210 ml. 1.0M Citric Acid-pH 3	Color comparison showed Fe concentration to be approx. the same throughout run, indicating no peak.	Fe = 41%
Fe-2	"	300 ml. 2.0M ammon. acetate pH 3	Visible Fe band remained at top of the resin column	Fe = No appreciable amt
Ba-1	100 mg Ba	307 ml. 2.0M ammon. acetate	Elutrient effluent sampled as follows: First 157 ml. contained 2% of the Ba Next 85 ml. " 5% " " " " 65 ml. " 13% " " "	Ba = 20%
Ba-2	"	300 ml. 1.0M Citric Acid-pH 3	Elutrient effluent sampled as follows: First 70 ml. contained none of the Ba. Next 81 ml. " 1.7% " " " " 82 ml. " 4.0% " " " " 67 ml. " 2.0% " " "	Ba=6.1%
Ba-8	10 mg. Ba + Ba "Tracer"	350 ml. 6N HCl	Elutrient effluent sampled as follows: First 150 ml. contained 24% of the Ba Next 100 ml. " 43% " " " " 50 ml. " 6% " " " " 50 ml. " 0.5% " " "	-
Ba-7*	0.047 mg/ml Ba + 5.0 mg/ml Pb + Ba "tracer" in 0.5M NaOH (Pb in solution as PbO ₂)		Ba "break-through" run. To date, no break-through had occurred, after passing approx. 3000 ml. of the feed solution through the 10 ml. resin column.	

* 10 ml. Dowex - "50" used in Run Ba-7.

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Table 6

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Run IR-7: Acetate - Citrate Ion Exchange Process For Ba¹⁴⁰
Purification

Conditions:

Column: IR-105 resin (40-60 mesh)

Resin volume = 25 ml.

Activation: Resin initially in NH_4^+ form with concentrated ammon. acetate.Feed: $\frac{1}{100}$ ionic scale of Ba¹⁴⁰ process.

0.5M ammon. acetate

vol. = 40.3 ml.

Flowrate: 0.55 ml/cm²/min.Procedure:

A. Run Feed on column

B. Wash with H₂O

C. Elute as follows:

Step I: 75 ml. 2.0M ammon. Acetate

" II: 230 ml. 1.0M citric acid, pH3

III: 150 ml. 6N HCl

Results:

Elution Step	% Cation In the Effluent					
	Ba	Pb	Fe	Ni	Cr	Sr
Feed effluent + H ₂ O wash	0.08	<10.25	50	12.3	4.4	(No analysis made for Sr)
I	0.14	33	8	20.3	3.9	
II	104	62	22	40	5.6	
III	1.5	<7.25	11	4.5	3.2	
Material Balance	105.7	112.5	91	77.1	17.1	(Sr)

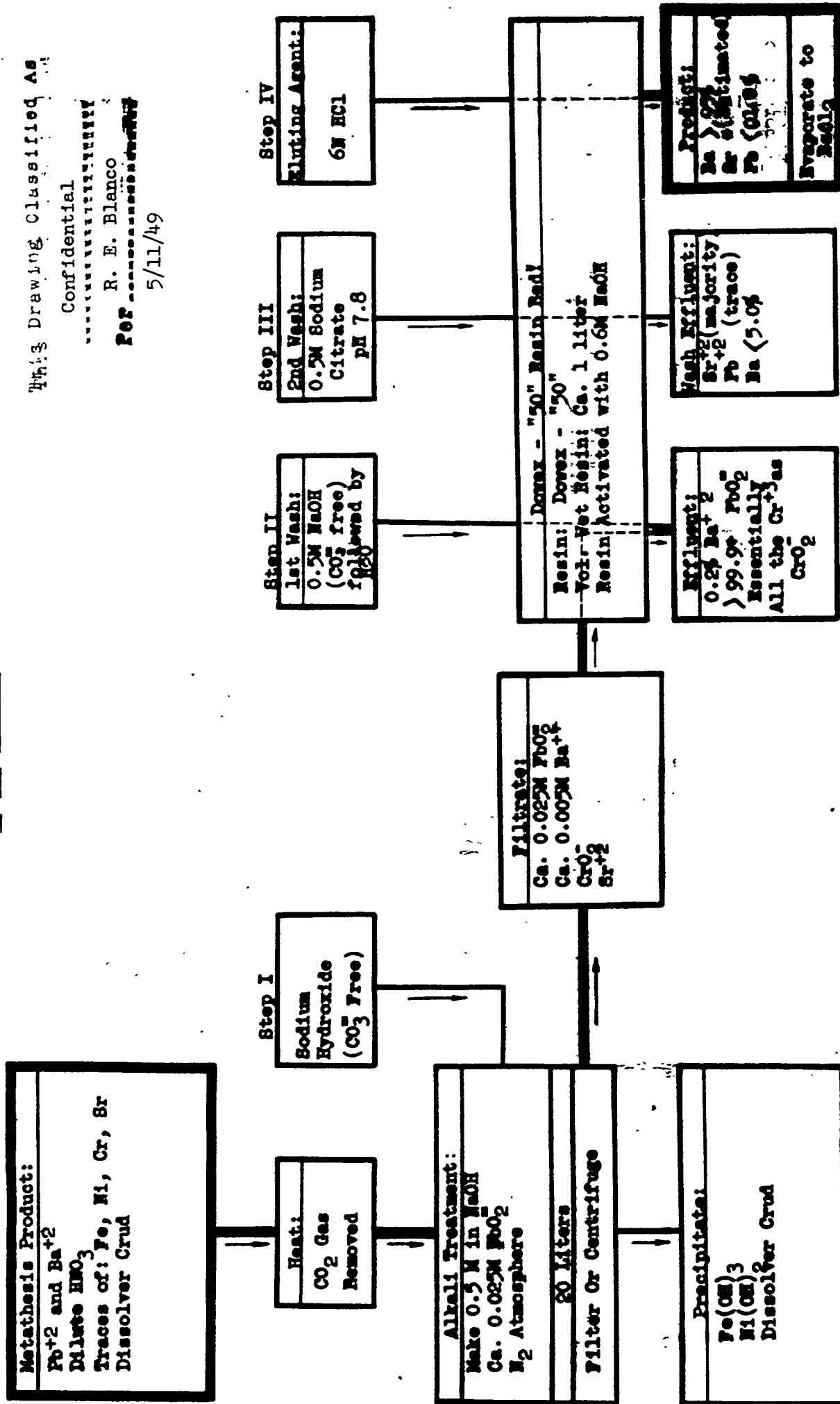
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Figure 1

Drawing No. 7191

Tentative Flowsheet: Alkali-Citrate Process For Ba Purification By Ion Exchange



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R. E. Blanco

Per

5/11/49

Volumes of washes and elutriant, geometry, and volume of column still under development.

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For R. E. Baerco
5/11/49

Fig. II

Separation of Ba and Pb by Elution with 1.0N Sodium Acetate - Run IR-10

Feed: 713 mg Pb + 2 - 100 mg Ba - 2

Conditions: IR-105 Resin, 40-50 mesh

Resin Vol. = 25 ml.

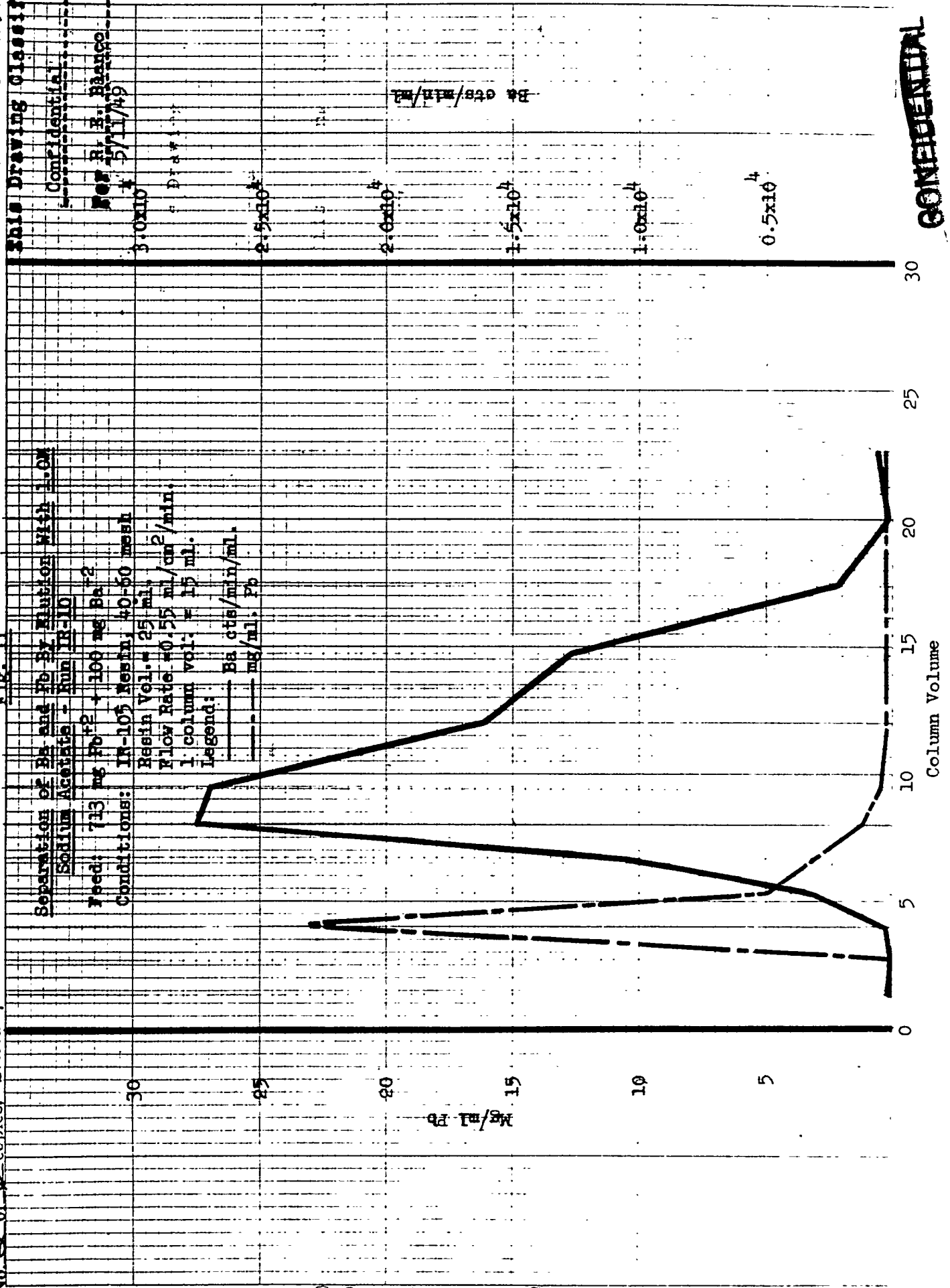
Flow Rate = 0.55 ml/cm²/min.

1. column vol. = 15 ml.

Legend:

— Ba cts/min/ml.

- - - mg/ml. Pb



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To: F. L. Steahly

Date: May 4, 1949

From: I. R. Higgins

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Problem No. TDSI-34

Part I

~~QUARTERLY~~
~~MONTHLY~~ REPORTTitle: Barium 140 Separation Development in the Semi-WorksWork by: I. R. Higgins, R. H. Vaughn, and W. A. HorneSUMMARY

One half scale equipment is being installed in Cell # 4 of the Semi-Works for demonstrating the barium 140 separation process through the metathesis step. Both filtration and centrifugation will be tried for replacing decantation to reduce mechanical losses of precipitate and to reduce time losses due to Ba¹⁴⁰ decay. It will also be determined if precipitate can be filtered or centrifuged from a higher concentration of uranium solution (40-50% vs. the 25% now employed) in the extraction step thus increasing production capacity. Equipment installation is nearly complete. Testing and cold runs should start by May 9.

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49-6-333

FLS-80

Technical Division
Chemical Process
Development Section

41

To: F. L. Steahly

Date: June 15, 1949

From: R. E. Blanco

Report Period: May 10- June 10, 1949

Distribution:

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M O N T H L Y _ R E P O R T

6. FLS

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey, G. C. Blalock

Secret Notebook No. CL-1656

SUMMARY

A tentative flowsheet was presented in the quarterly report ending May 10, 1949 for the purification of Ba¹⁴⁰ by an ion exchange process subsequent to the present metathesis step. An attempt has been made to develop an up flow resin column for use in this process so that if gas is formed as a result of water decomposition from radiation, the bubbles could escape and thus not block the column. An investigation of bed expansion as a function of resin mesh size and up flow rate was made. Resin sizes smaller than 200-240 mesh were found to be impractical. A resin bed was prepared for further study containing known percentages of resin mesh size varying from 40 to 240 mesh where the bed expansion was 25% for a flow rate of 0.56 cc/cm². ~~The theory of was 25% for a flow rate of 0.56 cc/cm²~~ The theory of such a column is that in up operations the large particles would remain at the bottom and each particle would assume a position relative to its size. Thus the bed would not "churn" and a chromatographic separation would be made possible. Duplicate runs made on up flow and down flow columns to separate Ba and Sr under flow sheet conditions (citrate elution) showed the product Ba obtained in the up flow column contained 14.4% of the Sr while the product Ba from down flow operation contained only 0.13% of the Sr. Further work on up flow columns will be deferred ~~XXXX~~

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(continued)

until a definite process has been developed by down flow methods.

The formation of a $\text{Ba}(\text{NO}_3)_2$ complex as reported in the literature was confirmed as it was found that 6N HNO_3 would remove Ba from a resin column 3 times as fast as 6N HCl .

Dowex 50 resin is stable in 0.5M NaOH -0.1M H_2O_2 solution. Traces of Pb in a solution of 5 mg/ml Pb in 0.5 NaOH are oxidized to PbO_2 when the H_2O_2 concentration exceeds 0.0001M. Traces of H_2O_2 will be present under process conditions as a result of decomposition of H_2O by radiation.

It was found that if the maximum amounts of Fe, Ni, and Cr expected to be present in the RaLa process are precipitated as the hydroxide they will carry 2 to 5% of the Ba. When Fe is present alone 85 to 99% of the Ba is carried where as if 5 mg/ml of Pb is present only 2% is carried. Washing the $\text{Fe}(\text{OH})_3$ with 0.5M NH_4NO_3 , pH 5.0 removes (recovers) the greater portion of the Ba from the precipitate. This system will be investigated further.

Experiments using Ba tracer have shown that the solubility of freshly precipitated BaSO_4 in 6-9M NaOH is at least 42 mg/100 ml of solution. The Ba remains in solution when the solution is diluted 10 times. As PbSO_4 is also soluble in NaOH , the possibility is suggested that the PbSO_4 - BaSO_4 precipitate obtained in the RaLa process could be dissolved in strong NaOH , diluted and passed onto an ion exchange column thus eliminating the metathesis, electrolyses, and ether hydrochloride steps.

Discussion:Up Flow v.s. Down Flow Columns.

In down flow ion exchange resin column, gas bubbles formed as a result of water decomposition by radiation will hamper operations and perhaps block the column entirely. For this reason up flow columns are being investigated so that any bubble formed could rise through the resin and escape. Chromatographic separations cannot be made if the resin particles are free to move i.e. "churn" in the column. To prevent this churning action a column containing a known graduation in resin particle size seemed desirable as in this case the larger resin particles would tend to stay at the bottom and in general all the particles would remain in a relative position according to their size. Experiments shown in Table I determined the % expansion of a resin bed as function of the liquid flow rate ^{and particle size} (up flow) for both water and 6N HCl. It was found that resin of particle size smaller than 200 mesh tended to "churn" and therefore should compose only a small fraction of an up flow bed.

a resin bed was made up as follows:

10 ml total - Dowex 50

20% 40-60 mesh

30% 60-80 mesh

20% 100-140 mesh

" 140-200 mesh

20% 200-240 mesh

Duplicate runs to determine the separation of Ba and Sr under the ~~XX~~ proposed flowsheet conditions were made on this up flow column and on a 10 ml, Dowex 50, 140-200 mesh down flow column. The results listed in Table II show that while the Ba obtained in the down flow column contained only 0.13% of the total amount of Sr the up flow Ba product contained 14.4% of the Sr. Although this is not a completely satisfactory separation the up flow column does show some merit and indications are that improved column design should increase the efficiency of separation. Further work on up flow operation

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until a definite process has been developed by down flow methods.

Elution of Ba with 6N HCL vs. 6N HNO₃

Duplicate runs were made to determine the relative efficiency of Ba elution with 6N HNO₃ or 6N HCl. It was found that 6N HNO₃ removed the Ba 3 times faster than the 6N HCl thus confirming the presence of a Ba(NO₃)₂ complex reported in the literature (See table 3).

Stability of Resin and Solutions in Alkaline Peroxide Solutions

The stability of resins and solutions in H₂O₂ are of interest ^{as} small amounts of H₂O₂ will be formed from the decomposition of H₂O by radiation. Dowex 50 resin which is normally considered to be a weak reducing agent was found to be stable in a solution of 0.1M H₂O₂ - 0.5M NaOH. This mixture was run through a down flow column (140-200 mesh, 1.5 cm diameter). Although bubbles formed in the resin the flow rate did not decrease appreciably.

A solution of 5 mg/ml of Pb as PbO₂⁻ in 0.5M NaOH was found to be unstable when the concentration of H₂O₂ exceeded 0.001M i.e. ^{traces of} ~~the~~ Pb ^{was} ~~is~~ oxidized to solid PbO₂.

Experiments are in progress to determine the possibility of forming the plumbate instead of the plumbite. H₂O₂ would not effect the oxidized form of Pb.

Carrying of Ba and Sr by the Hydrous Oxides of Fe, Cr, Ni and PbO₂

The flowsheet for Ba¹⁴⁰ purification calls for the removal of Fe, Cr, and Ni from the alkaline solution by centrifugation so that it is necessary to determine the amount of Ba lost (carried in this operation). The results of such an investigation are shown in Table 4. It is seen that (1) when all the ions are present in their maximum expected amounts that 2 to 5% of the Ba is carried (2). When Fe is present alone 85 to 99% of the Ba is carried. The presence of large amounts of Pb apparently inhibit the carrying of Ba by Fe(OH)₃. (3) PbO₂ formed by the oxidation Pb⁺² to PbO₂ with H₂O₂ carries

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about 50% of the Ba. (4) Relatively small amounts of Ba (1% or less) are carried by the $\text{Cr}(\text{OH})_3$ or $\text{Ni}(\text{OH})_2$.

The effect of NaOH concentration on the carrying of Sr by $\text{Fe}(\text{OH})_3$ is shown in Table 5. (Unfortunately the Ba analyses are not available). Ba would be expected to act similarly, however.

It appears that much less Ba is carried at 6M and 9M NaOH than at 0.25M to 0.75M. However, the evidence is not conclusive as the efficiency of Fe removal by centrifuging at these high molarities is poor due to the formation of ferrites and/or colloidal $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. Runs Xi and XIII where 2.5% and 80% of the Sr were carried respectively indicate again the effect of the presence of a large amount of Pb. Run XVII in comparison illustrates the effect of washing the $\text{Fe}(\text{OH})_3$ ppt. with pH 5 NH_4NO_3 . It is seen that about 77% of the Sr is recovered from the ppt. This confirms results reported by J. D. Karbitov et al where he states that Ba and Sr are carried by $\text{Fe}(\text{OH})_3$ ^{alone} but not below a pH of about 6.

Solubility of Freshly Precipitated BaSO_4 in 6-9M and 0.6-0.9M NaOH

The following experiments show that the solubility of freshly precipitated BaSO_4 in 6-9M NaOH is at least 42 mg/100 ml of solution.

- (1) Precipitated 10 mg Ba + tracer as sulfate, centrifuge, wash, and centrifuge
total Ba cts in ppt = 1.02×10^6
- (2) Dissolve ppt. in 40 ml of 9M NaOH (CO_3^{2-} free) and centrifuge,
total Ba cts in solution = 1.05×10^{63}
- (3) Dilute the solution to 400 ml
total Ba cts. in solution = 9.32×10^5

Another experiment showed the solubility of BaSO_4 at 6M NaOH to be similar. PbSO_4 is known to be soluble in 3-5M NaOH.

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Table 1

Expansion of Resin Bed in Up-Flow Column As A Function Of Flow Rate and Particle Size

Conditions: Column Diameter = 1.5 cm.
Resin: Dowex - "50"
Resin volume = 10 ml.
% Expansion calculated for Both H₂O and 6N HCl.

Resin Mesh	Flow rate (ml/cm ² /min.)	% Bed Expansion with H ₂ O	% Bed Expansion with 6N HCl
100-140	0.28 0.43 0.57 1.14 1.70 2.27	4.5 7.8 11.1 18.9 26.2 35	1 2 4 20 30 38.8
140-200	0.28 0.43 0.57 1.14 1.70 2.27	3.2 6.3 15.0 22.2 30.8 46.8	2.1 4.3 8.7 19 29 41
(Graded): 100=1.5% 100-140= 34% 140-200= 41% 200-230= 8% 230-325=11.5% 325= 4%	0.28 0.43 0.57	71.5 114 186	50 83.5 116.5

*Resin smaller than 200 mesh tends to "churn" and definite % of expansion cannot be accurately determined.

Table 2

Comparison of Separation of Ba and Sr by Up-Flow and Down-Flow
Ion Exchange Columns

Conditions:

Run Ba 17-Up Flow Column - Dowex 50 resin -10 ml total
 20% 40-60 mesh
 30% 60-80 mesh
 20% 100-140 mesh
 20% 140-200 mesh
 10% 200-240 mesh

Bed Expansion at flow rate $0.56 \text{ cc/cm}^2 = 25\%$

Run Ba 16 - Down-flow column - Dowex 50 resin, 10 ml, 140-200 mesh
 Both Runs - Activation: Resin initially put in Na form with $0.5M \text{ NaOH}$ (CO_3 free)
 Feed: 200ml of $0.5M \text{ NaOH}$ (CO_3 free)

1 gm. Pb as PbO_2

10 mg Ba and 1 mg Sr + Ba and Sr spike

Washes: I 30 ml $0.5M \text{ NaOH}$ (CO_3 free) followed by 30 ml H_2O

II 200 ml $0.1M$ sodium citrate pH 9.0

Ba Elutriant: 300 ml $6N \text{ HCl}$

Run No.	% Sr in 2nd Wash	% Ba in 2nd Wash	% Sr in Product	% Ba in Product	Sr Material Balance	Ba Material Balance
Ba 16	149.4	< 0.8	0.13	90.84	149.6	91.00
Ba 17	83.2	22.6	14.4	64	101.2	86.75

Table 3

Comparative Efficiencies Of 6N HCl and 6N HNO₃ As Eluting Agents
For Ba.

Conditions:

Resin: Dowex - "50" (140-200 mesh)

Resin volume = 10 ml.

Feed: 10 mg. "cold"Ba + Ba tracer

Feed volume = 20 ml.

Eluting agent effluent sampled periodically, as shown below.

Vol. of Effluent Sample (ml.)	% Ba Eluted with 6N HNO ₃	% Ba Eluted with 6N HCl
50	29.3	} 24.3
50	80.3	
50	.63	
50	-	32.0
50	-	11.5
50	-	6.2
50	-	.46
Mat'l Balance	109.6%	74.46%

Table 4

Carrying of Ba and Sr By Fe, Cr and Ni Hydroxides and PbO_2

Conditions:

CO_3 - Free NaOH and Boiled H_2O used in all cases.

Feed vol. = 40 ml.; 0.25 M NaOH; pH = 11.3

Feed solutions centrifuged and precipitates washed with 3-15 ml.

volumes 0.5M CO_3 - Free NaOH, followed by 1-30 ml. H_2O wash

Precipitates dissolved in 3N HNO_3 for final analysis

Run No.	Cation Concentration In Feed Solution	% Ba Carried	% Sr Carried
I	200 mg. Fe; 0.45 mg. Cr; 0.34 mg. Ni; 1.88 mg. Ba; 0.22 mg Sr; 207.1 mg Pb	5.3	10.9
I-C	"	2.5	7.0
II	" + 0.1 M H_2O_2	50	39
III	201.7 mg Pb + "	44	36.8
IV	0.68 mg Ni	0.26	0.2
V	201.7 mg Pb; 0.45 mg Cr	1.2	5.32
VI	0.48 mg Fe	85.8	73.2
VII	1.0 mg Fe	90.05	83.3
VIII	2.0 mg Fe	97	98
VIII-c	" "	94	96.3
IX	4.0 mg Fe	99.14	97.4

Table 5

Carrying of Sr By $\text{Fe}(\text{OH})_3$ at Varying NaOH Concentrations

Conditions:

CO_3^{2-} - Free NaOH and boiled H_2O used in all cases.
 Feed vol. = 40 ml.; *1 mg. Fe^{+3} , Ba Tracer
 Feed solutions centrifuged and precipitates washed with 3-15 ml. vol. -
 umes 0.5M CO_3 - Free NaOH, followed by 1-30 ml. H_2O wash.
 Precipitates dissolved in 3N HNO_3 for final analysis.

Run No.	Molarity NaOH	% Sr Carried	
*XI	0.25M	2.5	
*XII	5.75M	7.17	
XIII	0.315M	80	
XIV	0.75 M	83	
XV	5.75 M	7.2	(centrifugate yellow)
XVI	8.75 M	0.45	(")
**XVII	0.25 M	3.2	

- * Runs XI and XII contain 201.7 mg Pb in addition to 1 mg. Fe.
- ** Run XVII - Washed with 2-15 ml. vols. 0.5M CO_3 - Free NaOH, followed with 30 ml. H_2O wash (wash 1), then washed with 2, 15 ml. vols. 0.5M NH_4NO_3 at pH 5, followed with 30 ml. H_2O wash (wash 2).

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49-7-281

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FLS-98
Technical Division
Chemical Process
Development Section

To: F. L. Steahly *FLS*

Date: July 11, 1949

From: R. E. Blanco

Report Period:

June 10 - July 10, 1949

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Part

MONTHLY REPORT

Title: Purification of Ba¹⁴⁰ By Ion Exchange

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Secret Notebook No. CL-1656

1.0 SUMMARY

Two ion exchange processes have been developed in an effort to eliminate the electrolysis and ether-hydrochloride extraction steps in the present RaLa process for Ba¹⁴⁰ purification. In the "Alkaline-Citrate" process, the feed is basic. Iron, nickel and chromium are precipitated as hydrous oxides and separated from the solution. The lead passes through the Dowex-"50" cation exchanger column as the plumbite while the barium and strontium are adsorbed on the resin. Strontium and sodium are selectively eluted, leaving the barium still held strongly on the column. The barium product is recovered by elution with 6 N Nitric acid. In the "Acetate-Citrate" process, the feed is 0.5 M in sodium acetate. ~~About~~ Part of the lead, along with 60-90% of the iron passes through the exchange bed. Selective elution of the remaining iron, nickel, ~~strontium~~ lead, strontium and sodium follows. The barium product is recovered in 6 N nitric acid. During the past month, major consideration has been given to refinements of the Alkaline process, especially adequate separation of strontium and sodium from the barium product.

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In both the above processes, a large amount of sodium is associated with the product. It has been suggested that the weight of sodium in the final product should not exceed the weight of the barium. It was found that a 6 N hydrochloric acid wash of the column, prior to barium elution, resulted in a Ca. 25-fold reduction in the amount of sodium present in the barium product so that the final ratio of Na: Ba was approximately 3. The barium loss in this washing step was less than 0.01%.

The use of IRC-50 resin is being investigated as a means of reducing the volume of acid used for elution of Ba product thus reducing evaporation volume.

Adequate separation of strontium from barium has been achieved by selective elution of strontium with sodium citrate at pH 7. The barium loss in this wash is about 0.03%.

A study of the efficiencies of nitric acid and hydrochloric acids as elutriants for barium has been made, and 6N nitric acid has been selected as the most satisfactory because of the relatively small volumes required.

The possibility of elimination of the metathesis step in the RaLa process by direct dissolution of the barium and lead sulfates in 6 M sodium hydroxide (CO_3 = free) before ion exchange treatment has been investigated. Experiments have also been carried out dealing with the separation of barium and lead as the carbonates immediately after metathesis. Success of this method depends upon the relative solubilities of Barium and lead carbonates in strong (4M) potassium carbonate or in a 0.5 M potassium carbonate solution, 6 M in potassium hydroxide.

Attempts to minimize the carrying of barium by the hydrous oxides in the precipitation step of the "Alkaline" process by use of ammonium nitrate, pH 5, as a washing agent have reduced the barium losses to less than 1% (in the presence of "cold" barium and/or lead).

2.0 Discussion

Separation of barium, strontium, and sodium by selective elution in both the "Alkaline-Citrate" and "Acetate-Citrate" processes for Ba¹⁴⁰ purification:

The separation of strontium and barium has been accomplished by selective elution of the strontium with 20 column volumes of 0.1 M Na-Citrate at pH 8. Essentially all of the Sr was eluted in this wash, with a barium loss of 0.03%. (See table 3). Since the Na⁺ replaces the Sr in this washing step and it is desirable to keep the amount of sodium remaining with the Ba product to a minimum (not to exceed the weight of the Ba) it has been necessary to devise a method for the adequate separation of sodium from barium. By washing the column with 6 N HCl until the effluent is acid + 3 column volumes excess immediately after the Sr. elution step, the sodium contamination of the barium product has been decreased ca. 25-fold with a barium loss of 0.05%. Under the best conditions, the final ratio of Na to Ba was 3. By using 0.5 M HCl, the Ba loss was 0.01% but the sodium concentration in the barium was about twice as great as when the 6 N acid was used. (See tables 1 and 2).

The substitution of IRC-"50" resin for Dowex -"50" in the "Alkaline" process is being considered. Use of IRC-"50" as a cation exchanger in this process appears favorable because: (1) Ba can be eluted in a very small volume of acid, thus reducing evaporation volumes, and (2) its exchange capacity is double that of Dowex -"50" and would therefore permit a 1/2 reduction in the size of the required resin bed. The sodium form of IRC-"50" undergoes hydrolysis fairly readily and, from this standpoint, may prove valuable in the separation of Na and Ba by water washing or by correct choice of a strictly controlled Buffer solution as a washing agent. Some preliminary cold runs have been made to determine the capacity of IRC-"50" for Na at varied conditions of pH. (see table 4). IRC-"50" resin would not be satisfactory for the "Acetate-Citrate" process (in which pH is alternately acid and basic) because it swells about 30% during conversion from H⁺ to Na⁺ form.

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Relative Efficiencies of 2 N HNO₃, 6 N HNO₃ and 6 N HCL as Eluting Agents For Ba

Three runs were made with Dowex-"50" resin using 2 N HNO₃, 6 N HNO₃ and 6 N HCL, respectively as an eluting agent for barium. (See fig. 1). In all cases the feed contained 10 mg. of barium as Ba(NO₃)₂ plus barium tracer. The resin was initially put in the H⁺ form. 100% of the Ba was eluted in the first 6 column volumes of 6 N HNO₃, whereas more than 32 column volumes of 6 N HCL were required for 100% Ba elution. Only 37% of the barium was eluted by a total of 32 column volumes of 2 N HNO₃.

Solubility of Ba and Pb Sulfates in NaOH

The possibility of eliminating the metathesis step in the present RaLa process by direct solution of the Ba and Pb sulfates in 6 M CO₃-free NaOH has been considered, and one laboratory run on 1/100 full process scale has been made. However, only a 40% Ba material balance was attained, and approximately 10 mr/hr of activity was left on the resin after elution of the Ba with a large excess of 6 N HNO₃. It is believed that the activity remaining on the resin was due to the "filtering" out of particles of undissolved, solid BaSO₄. (See table 2). Other investigations were made in an effort to determine the relative solubilities of Ba and Pb sulfates in various concentrations of CO₃ free NaOH. It was found that colored, higher oxides of lead which are insoluble on subsequent dilution to 6 M NaOH, are obtained when strong (18.6 M) NaOH. However, if 6 M NaOH is initially used as the solvent for PbSO₄, a white lead oxide is obtained that is soluble on dilution to 3 M NaOH, ^{solid PbSO₄ is not converted} if the initial solvent used is 3 M NaOH, a white insoluble lead oxide is obtained that will not dissolve on further dilution. It was also found that BaSO₄ is only slightly soluble in 3 M NaOH.

In order to identify the components of the insoluble salts of Ba and Pb in 6 N NaOH, a tracer experimental run was made as follows:

(1) ppt as SO_4 = ; 100 mg Pb, (wash with H_2O) 10 mg Ba 1 mg Sr	Total cts Ba 6.592×10^6 Sr 6.591×10^6 (in precipitate)
(2) Dissolve in 35 ml of 6 M NaOH (CO_3 free) Centrifuge → trace of ppt Dissolve ppt in HNO_3	2.28×10^3 1.32×10^3 (in precipitate)
(3) Dilute to 420 ml with boiled H_2O (cloudy)	6.59×10^6 6.59×10^6 (in cloudy solution)
(4) Centrifuge	6.46×10^6 7.56×10^6 (in clear supernate)

These results indicate that the Ba SO_4 is soluble and that therefore the ppt is a Pb compound.

Separation of BaCO_3 from Pb^{+2} by Centrifugation

It is known that Ba CO_3 is relatively insoluble in con. alkaline carbonate solutions while Pb CO_3 is soluble. It may be possible to make use of this difference in solubility and separate the Ba CO_3 from the Pb^{++} by centrifugation. The small amount of Ba present (1 gm) may prohibit a high centrifuge efficiency. Tracer experiments were run using a laboratory clinical centrifuge (ca. 2650 RPM) and 1 hr. centrifugation periods to determine the % of Ba lost in the supernate. When the Ba - Pb CO_3 ppt was treated with 4 M K_2CO_3 , 13% of the Ba was found in the supernate. When 0.5 M K_2CO_3 , 6 M NaOH was used, 7.9% of the Ba was in the supernate. It is not known whether the Ba was in solution or in fine suspension. (see table 5).

Carrying of Ba and Sr by $\text{Fe}(\text{OH})_3$

It has been found the carrying of Ba and Sr on $\text{Fe}(\text{OH})_3$ varies inversely with the con. of cold Ba and Pb. Under process conditions 1 mg. of Fe would carry 5.0% of the Ba in the presence of 1 gm of Ba and 0.7% in the presence of 100 gms of Pb and 1 gm of Ba. Washing the $\text{Fe}(\text{OH})_3$ ppt. with 0.5 M NH_4 acetate, ph 5, reduces the amount carried to 1% and 0.1% respectively.

(See table 6)

TABLE I

Separation of Ba and Na By Washing Dowex -"50" Column With HCl

Conditions:

Column: 10 ml. Dowex "50" Resin, 140-200 mesh
Resin initially in Na^+ form, activated with conc. NaCl solution

Feed: 10 mg. Ba

10 ml. Ba "tracer"

0.1 M NaOH to neutralize

Dilute to 25 ml. with H_2O (i.e. $\text{Na}^+ = \text{ca. } 0.92 \text{ M}$)

Washes: (1) HCl until effluent is acid - (See conc. in table below)
(2) 12 ml. H_2O - to flush out bed "hold-up"

Elution: of Ba Product: 100 ml. 6 N HNO_3

Flow Rate: 0.55 ml/cm²/min.

Run No.	Conc. of HCl Wash	% Ba		Mg. Na		Mg. Ba in HNO_3 Product	Mg. Na in HNO_3 Product	Ba Material Balance
		HCl Wash	H_2O Wash	HCl Wash	H_2O Wash			
Ba-I	6 N	0.05	0.009	611	238	710.0	33.9	ca. 126%
Ba-II	0.5 N	0.01	0.002	7.3	7.33	10.0	69.8	ca. 100%

TABLE II

Separation of Ba, Sr and Pb By Selective Elution in Basic-Process For Ba¹⁴⁰ Purification

Run Ba-22:

Conditions: Column: 10 ml. Dowex -"50" Resin, 140-200 mesh
Resin initially in Na⁺ Form with 0.5 M CO₃ - Free NaOH

Feed: 500 mg. Pb
10 mg. "cold" Ba
1 mg. "cold" Sr

Precipitation of Feed:
10 mg. Ba "tracer", containing "tracer" Sr

Precipitate Ba, Sr and Pb as sulfates with 1:1 H₂SO₄
Centrifuge and Decant
Wash, by centrifuging and decanting with 3.25 ml. volumes H₂O
Combine all supernates.
Dissolve precipitate in 6 M NaOH and dilute to 0.5 M NaOH with
balled H₂O. (Use CO₃ - Free NaOH)

Run of column at flow rate = 0.55 ml/cm²/min

Column Washes:

- (1) 25 ml. 0.5 M CO₃ - Free NaOH, followed by 30 ml. H₂O
- (2) 20 ml. 0.1 M HNO₃, Followed by 30 ml. H₂O
- (3) 200 ml. 0.1 M Na Citrate, pH₈, followed by 30 ml. H₂O
- (4) 6 N HCl until effluent is acid.

Elution of Ba Product: 100 ml. 6 N HNO₃

Cation Eluted	Cation In Supernates From Precipitation	Cation In Column Effluent From Feed + Washes (1) and (2)	Cation In Wash (3) - (0.5 M Na Citrate pH ₈)	Cation In Wash (4) (6N HCl)	Cation In Ba Product (6 N HNO ₃)	Material Balance
Pb	—	Essentially all	0.085%	0.008%	40.0%	40.2%*
Ba	0.085%	0.022%	80.33%	0.051%	0.67%	83.3%
Sr	2.10%	0.123%	—	670 mg.	63.2 mg	—
Na	—	—	—	—	—	—

* Ca. 10 mr/hr of activity was left in the column, probably as insoluble sulfates

TABLE III

Ionic Separations By Selective Elution In Acetate-Citrate Process For Ba¹⁴⁰ Purification

Run Ba-19:

Conditions: Column: 10 ml. Dowex "50" Resin, 140-200 mesh
 Resin initially put in Na⁺ form with 0.5 M Na Acetate
 Feed: 10 mg. Ba; 1.0 mg. Sr; 10.0 mg. Fe; 50.0 mg. Pb; 2.08 mg. Cr;
 1.68 mg. Ni⁺⁺
 Ba "tracer"; containing "tracer" Sr. Ba=1.35 x 10⁷ total counts
 Sr = 1.15 x 10⁷

Volume = 50 ml.

Flow Rate: 0.55 ml/km²/min.

Eluting Agents:

- (1) 30 ml. 0.5 M NaOH (CO₃-Free)
- (2) 50 ml. 0.5 M Na Citrate, pH₃
- (3) 165 ml. 0.1 M Na Citrate, pH₉
- (4) 300 ml. 6 N HNO₃ (Ba product)

Cation Eluted	% of Cation in feed effluent	% of Cation Selectively Eluted				Material Balance (%)
		(1) 0.5 M NaOH (CO ₃ - Free)	(2) 0.5 M NaCit pH ₃	(3) 0.1 M NaCit pH ₉	(4) 6N HNO ₃ (Ba Product)	
Ba	0.02	0.0053	0.02	0.03	88.8	88.85
Sr	0.02	0.0070	0.02	104.14	0.2	104.36
Pb	—	32	—	—	2.4	—
Ni	7.5	—	—	—	< 15.0	—
Fe	61.7	—	18	—	< 1.0	ca. 80.7
Cr	35	—	—	—	< 12.0	—

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TABLE IV

Na Capacity of "IRC-50" Resin with Varying pHConditions:

Column: 5 ml. Dry "IRC-50" Resin

Activation: (1) Down-flow: 25 ml. 1.0 M HCl; 10 ml. H₂O(2) Up-flow: 1.0 M CO₃-Free NaOH until effluent is Basic +
**20 ml. Excess; **50 ml. H₂O (Down-Flow)Wash Down-Flow:

(1) *Wash until wash effluent and feed are same pH - (See table).

(2) 50 ml. H₂O

Elution of Na: 20 ml. 1.0 M HCl

Na Product taken to dryness at 110°C and weighed as NaCl

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Run No.	Wash Solution	pH Wash	Resin Capacity For Na (mg)
C-1	—	*	174.2
C-2	0.1 M Na-Citrate	9	572.7
C-3	1.0 M Na-Acetate	5	109.7
C-4	"	4	26.9
C-5	"	3.7	12.4
C-6	—	*	524.0

** In Run C-6, ca. 235 ml. excess of NaOH was used and only ca. 20 ml. H₂O wash* In Runs C-1 and C-6 no Buffer Wash was used - H₂O effluent slightly alkaline because of hydrolysis of Na⁺ - form of the Resin.

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TABLE V

Separation of BaCO_3 from Pb^{+2} by Centrifugation

Conditions:

Feed: 2.85 mg "cold" Ba
160.5 mg Pb
5.0 ml 0.1 M Ba "tracer"

Procedure: Precipitation made with 40 ml. 1.0 M K_2CO_3

Centrifuge; Decant

Wash with 1, 40 ml. volume H_2O

Centrifuge 1 hour; decant. (2650 R.P.M. Lab. centrifuge)

Dissolve precipitate as shown in Table, Below.

Run No.	Solvent used for PbCO_3	% Ba Dissolved with the Pb
I	40 ml. 0.5 M K_2CO_3 6 M. in KOH	7.95
II	40 ml. 4.0 M K_2CO_3	13.19

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TABLE VI

Carrying of Ba and Sr By the Oxides of Fe and Pb; Effectiveness of pH5 NH_4NO_3 as Washing Agent For The Oxide-Precipitates

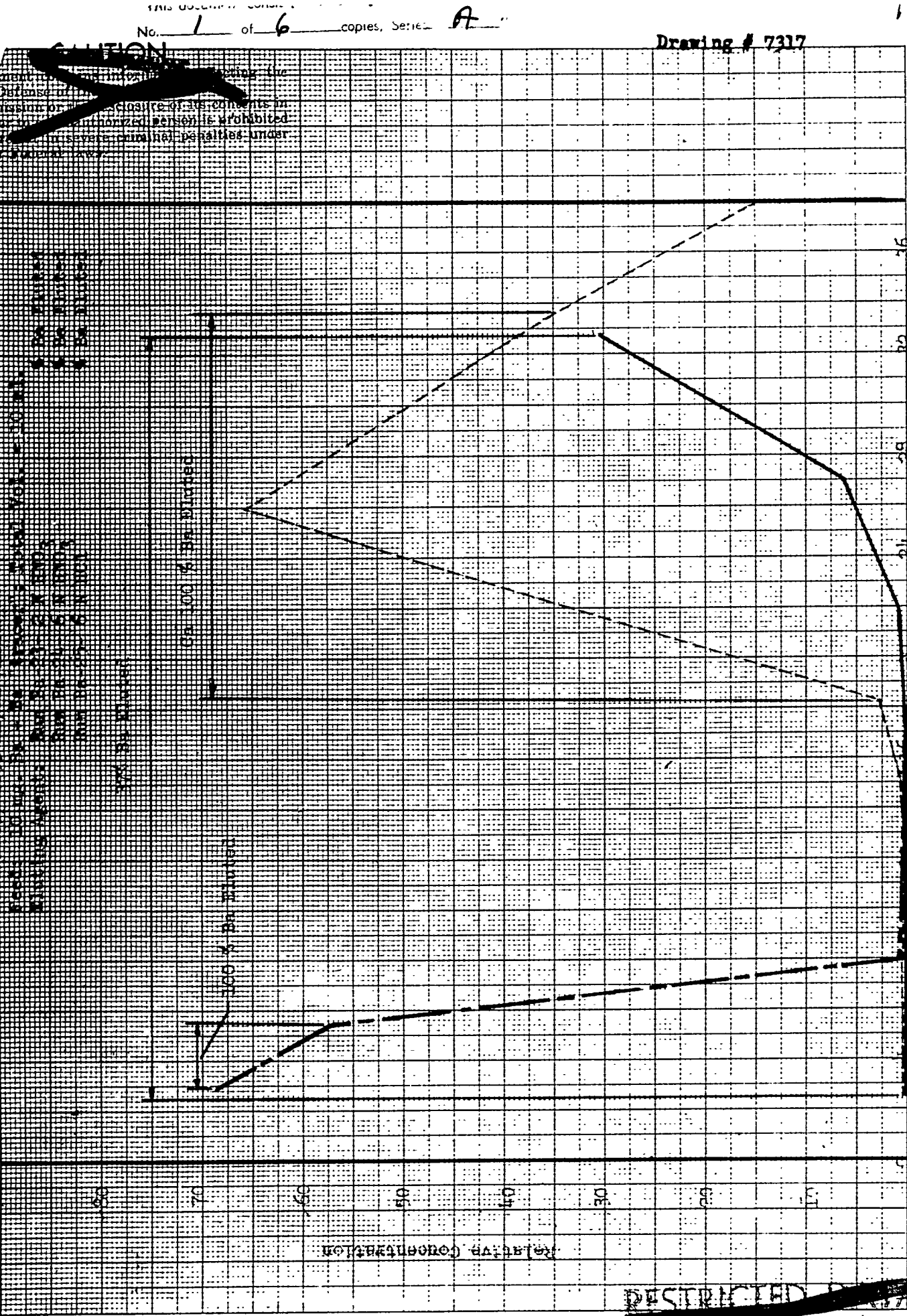
Conditions: CO_3 -Free NaOH and Boiled H_2O used in all precipitations, dilutions and washes. Cations precipitated from 0.25 M CO_3 - Free NaOH, pH 11.3, in all cases.
Feed: Runs III, VII, XI, and XVII contain No "Cold" Ba
Washes: All precipitates washed with *3.15 ml. volumes 0.5 M CO_3 - Free NaOH followed by 1.30 ml. volume of H_2O before proceeding as follows:
Runs III, VII, and XI: use No NH_4NO_3 , pH5 wash.
Run XVII: Use 2.15 ml. volume NH_4NO_3 , pH5 wash, then 30 ml. H_2O .
Runs XVIII and XIX: Use 3 ml. volumes NH_4NO_3 , pH5 wash, then 30 ml. H_2O .
All precipitates were dissolved in 3 N HNO_3 for final analysis.

Run No.	Cation Concentrations in Feed Solutions	% Ba		carried by ppt.	% Sr		Carried by ppt.
		In NaOH Wash	In NH_4NO_3 Wash		In NaOH Wash	NH_4NO_3 (ph 5) Wash	
III	201.7 mg. Pb, 0.1 M H_2O_2 + Ba and Sr tracers	56	—	44	63.2	—	36.8
VII	1.0 mg. Fe + Ba and Sr Tracers	9.95	—	90.05	16.44	—	83.3
XI	1.0 mg. Fe + 201.7 mg. Pb + Ba and Sr tracers	—	—	—	97.15	—	2.48
XVII	1.0 mg. Fe + Ba and Sr Tracers	—	—	—	18.15	78.93	3.2
XVIII	1.0 mg. Fe + 10 mg. "cold" Ba + Ba tracer	94.4	4.54	0.97	98.82	1.03	0.07
XIX	1.0 mg. Fe + 100.5 mg Pb + 10 mg. "cold Ba + Ba Tracer	99.3	0.56	0.10	99.6	0.33	0.02

* In Run XVII only 2.15 ml. volumes of 0.5 M CO_3 - Free NaOH were used as wash.

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ELUTION OF Ba WITH N HNO₃ and 6 N HCl
Conditions: Resin: 10 ml. Dowex - 50, 140-200 mesh, initially in H⁺ form.
1 Col. Vol. = 6 ml.
Flow Rate: 0.55 ml/cm²/min.
Peak Volume: 100 ml. Ba Eluted
Elution Volume: 100 ml. Ba Eluted
Elution Volume: 100 ml. Ba Eluted



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Eluate In Column Volumes

Technical Division
Chemical Process
Development Section

To: F. L. Steahly

Date: August 19, 1949

From: R. E. Blanco

Report Period: 5/10/49-8/10/49

Distribution: (1) FLS, (2) WKE, (3) REB, (4) FRB, (5) JOD, (6) FLS, (7) WEU

Problem No. TDSI-30

Part 1

QUARTERLY REPORT

This document consists of 11 pages and 0 figures. No. 1 of 7 copies, Series M

Title: Purification of Ba^{140} by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey, G. C. Blalock

Secret Notebook No. CL-2041, CL-1656

SUMMARY

Ion exchange is being considered for use in the RaLa process as it offers the advantages of ease of remote control and higher purity of product. Two ion exchange processes have been developed for the purification and recovery of Ba^{140} subsequent to either the lead sulfate precipitation step or the metathesis step replacing the metathesis, electrolysis and ether hydrochloride steps.

In the Acetate-Citrate Process the barium-lead sulfate precipitate is dissolved in 1M sodium acetate or the acid metathesis product is made 0.05 M in sodium acetate and passed through a Dowex 50 resin column where the Br, Sr, and Pb are adsorbed while most of the Fe and Cr pass through as acetate complexes. The Pb, Fe, Sr, and Na are selectively eluted and the pure Ba finally eluted in 6 N HNO_3 with a yield of approximately 99%. In the Alkali-Citrate Process the barium-lead sulfate is dissolved in 6 M NaOH ($CO_3^{=}$ free), diluted to 0.6 M NaOH or the acid metathesis product is made 0.5 M in NaOH, centrifuged to remove the hydrous oxides of Fe, Cr, and Ni, and passed through the resin. The Pb passes through as the plumbite and Ba is freed from Sr and recovered as above. These processes have been verified in the laboratory on 1/100 scale and are now in pilot plant trial on full scale (see flowsheet Figure I).

The elution curves of Ba with 6 N HNO_3 v.s. 6 N HCl or 2 N HNO_3 are plotted in Figure II and show the former to be about eight times as efficient due to the complexing action of the nitrate. This also shows why a large amount of 6 N HCl can be used to selectively elute the Na from a column with a negligible Ba loss.

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If the maximum amounts of Fe, Ni, and Cr expected to be present in the RaLa process are precipitated as the hydroxide ^{in the} with Alkali-Citrate Process, they will carry 2-5% of the Ba. However, the use of ammonium nitrate, pH 5, as a washing agent will reduce the loss to less than 1%.

Laboratory experiments have shown that approximately 99% of the impurities, Fe, Cr, Ni, and possibly Pb, can be separated from Ba by adsorption on the acetate form of IR4B or Dowex A2 anion resin from a 0.5 M Na acetate solution.

An attempt is being made to develop an up flow resin column so that if gas is formed as a result of water decomposition from radiation, the bubbles could escape and thus not block the column. After an investigation of bed expansion as a function of particle size and up flow rate was made, a resin column was prepared containing known percentages of particles ranging from 40-240 mesh where the bed expansion was 25% for a flow rate of 0.56 cc/cm²/min. During operation each particle assumes a position relative to its size so that the bed does not "churn". An encouraging separation of Sr and Ba has been made with this column.

The use of IRC-50 resin is being investigated as the volume of acid needed for Ba elution would be considerably less thus reducing evaporation volume. Two disadvantages are: (1) Ba and Sr are held much more strongly on IRC-50 than Dowex 50 and thus a much larger volume of citrate elutriant is needed. Also, the degree of separation of Ba and Sr is poor so that a new acid elution process will have to be developed; (2) Since H⁺ ion replaces all other cations, HCl cannot be used to separate Na and Ba. The change in capacity of the resin for Na with pH has been determined (see Figure III) so that by washing the resin with sodium acetate of the proper pH (ca. 4.0), it is expected that the bulk of the Na will be separated from the Ba.

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Alkali-Citrate Process Development

An ion exchange process for Ba¹⁴⁰ purification was presented in the monthly report ending July 10 where by the Ba and Pb sulfates were dissolved in 6 N NaOH (CO₃ free), diluted to 0.6 M NaOH and the solution passed through a resin column. After selectively eluting the Sr with pH 9 Na citrate and the Na with 6 N HCl, the Ba was removed with 6 N HNO₃. (See flowsheet, Figure I.) The first laboratory run on 1/100 scale showed a poor Ba material balance. This run has been repeated showing a 99⁺% yield of Ba containing only 0.08% of the Sr. The efficiency of a 6 N HCl wash for Na removal is shown by the low ratio of Na to Ba in the product i.e. Na/Ba = 0.08 (see Table I). Since 6 N HCl is so corrosive, 0.5 and 1.0 M acetic acid have been tried unsuccessfully as eluting agents for the separation of Na from Ba.

Acetate-Citrate Process Development

It has been shown that at least 10 mg of Ba and 1 gm of Pb as the sulfates can be dissolved in 200 ml of 1 M Na acetate. Such a solution containing Ba and Sr tracer and impurities on 1/100 the RaLa scale was passed through a resin column. The column was then washed with NaOH, Na citrate at pH's 3 and 9, and 6 N HCl ^{RESPECTIVELY,} to ^{LOW} selectively remove the Pb, Fe, Sr, and Na before the Ba elution with 6 N HNO₃ (see Figure I for flowsheet). The results were not conclusive in that both the Ba and Sr were eluted earlier in the process than expected (see Table II). This phenomenon is a result of the large amount of NH₄ acetate present in the feed. As a result, the Ba and Sr are caught at the bottom of the column instead of the top and thus are eluted too soon. In fact, 24% of the Sr came through in the feed effluent. This condition will be corrected in a re-run by using twice as much resin. It should be noted that the Ba, Sr, and Pb were in true solution in

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the feed or they would not have been adsorbed on the resin.

Separation of Fe, Cr, Na, and Pb from Ba by Anion Exchange Process

Laboratory experiments have shown that approximately 99% of the Fe, Cr, Ni, and Pb can be removed from a Ba solution by adsorption on an anion resin column. The procedure was as follows: A 0.5 M Na acetate solution pH 5.5-6.0 containing 10 mg each of Fe, Cr, and Ni; 50 mg of Pb, 10 mg of Ba, and 1 mg of Sr plus tracer Ba and Sr was passed through an anion resin column which had been activated with 0.5 M Na acetate pH 8.2. The column was then washed with 100 ml of H₂O or 0.5 M Na acetate pH 6. At least 86% of the Ba and 100% of the Sr pass through the column while the other impurities are caught (see Table 3).

Three possible mechanisms to explain this reaction are as follows:

(1) that anion acetate complexes are formed and adsorbed as such; (2) that the weak base IR 4B anion resin or the medium base Dowex A2 anion resin are sufficiently hydrolyzed at these high pH's so that the hydroxides of the Fe, Cr, Ni, and Pb are precipitated on the resin particles; or (3) that the hydrous oxides or acetates are adsorbed as colloids. Further runs will be made to verify these results. Application of this process to the acetate-citrate Ba¹⁴⁰ purification would result in a considerable saving of time as the feed could be passed through the anion column for impurity removal and then to the cation column for separation of Sr and Na from Ba.

Investigation of IRC-50 Resin

The variation of the Na capacity of IRC-50 resin with pH of solution is shown in Figure 3. If this resin were used in the RaLa process it is planned to take advantage of this relationship to obtain the separation of Ba and Na.

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If acid is passed through on IRC-50 column containing adsorbed Ba and Na, the resin is immediately transformed to the H^+ form thus eluting the Ba and Na together. However, by washing with a buffer solution of 1.0 M Na acetate of the proper pH, the bulk of the Na will be replaced by H^+ and the remaining space occupied by Ba, as Ba is held stronger than Na. Thus when the Ba is eluted with acid, the amount of Na present will be very small. This system was tried using pH 3.7, 1.0 M Na acetate. It was found that the Ba was removed at this pH, however, so that subsequent runs will be made at pH's 4.0, 4.2, etc.

It has been found that Ba and Sr are held much more strongly by the IRC-50 resin than Dowex 50 i.e. it takes 150 ml of 0.1 M Na citrate pH 9 to remove the Sr from 10 ml of Dowex 50 while it takes 380 ml of 0.3 M pH 9 citrate to remove the Sr from 5 ml of IRC-50. Also, in the latter case the separation from Ba is not satisfactory.

The amount of hydrolysis of the Na form of IRC-50 during the washing of the column by deionized water has been found to be approximately 6 mg of Na/100 ml of H_2O /5 ml of dry, H^+ form of IRC-50 resin.

IRC-50 resin (H^+ form) was found to be stable for at least 24 hours in 6 N HNO_3 . However, when the Na form was converted to the H^+ form with 6 N HNO_3 the resin turned pink and would not decolorize on regeneration with 1 M NaOH. IRC-50 was stable at room temperature in 1 M NaOH but turned yellow-brown in boiling 1 M NaOH and smelled of naphthalene.

Purification of Ba¹⁴⁰ by Ion Exchange Following Dissolution of Ba-Pb
Sulfates in 6 M NaOH (CO₃⁼ free)

Run Ba-26

Conditions: Column:: 10 ml Dowex-50 resin, 140-200 mesh, resin initially in Na⁺ form with 0.5 M NaOH

Feed: 500 mg Pb
10 mg Ba + tracer
1 mg Sr + tracer

Feed Preparation:

Precipitate Ba, Sr, and Pb as sulfates with 1:1 H₂SO₄; centrifuge; wash with 3-25 ml volumes H₂O
Dissolve precipitate in 6 M NaOH (CO₃⁼ free) and dilute to 0.05 NaOH with boiled H₂O

Flow Rate: 0.55 ml/cm²/min

Column washes:

- (1) 25 ml 0.5 M NaOH (CO₃⁼ free) followed by 30 ml H₂O
- (2) 20 ml 0.1 M HNO₃, followed by 30 ml H₂O
- (3) 200 ml 0.1 M Na citrate, pH 9, followed by 30 ml H₂O
- (4) 25 ml 6 N HCl

Elution of Ba Product: 45 ml 6 N HNO₃

Cation Eluted	Cation in Supernates from Precipitation	Cation in Column Effluent From feed + Washes (1) and (2)	% Cation in Wash (3)	% Cation in Wash (4)	% Cation in Ba product	% Mat'l Balance
Pb	-	Essentially All	-	-	-	-
Na	-	-	-	99.91	0.09	-
Sr	7.8%	0.25	85.33	0.64	0.08	94.1
Ba	0.12%	0.10	0.26	0.08	109.1	109.6

Table I~~x~~

Purification of Ba¹⁴⁰ by Ion Exchange Following Dissolution of Ba-Pb Sulfates
In 1 M Na Acetate

Run Ba-28

Conditions: 10 ml Dowex-50 resin, 140-200 mesh, resin initially in Na form

Feed:	10 mg Ba + tracer	10 mg Fe
	1 mg Sr + tracer	2 mg Cr
	1000 mg Pb	1.7 mg Ni

Feed Preparation:

Precipitate Ba, Sr, and Pb as sulfates with 1:1 H₂SO₄
 Centrifuge; wash with 3-25 ml volumes H₂O
 Add Fe, Cr, and Ni
 Dissolve ppt. in 250 ml 0.5 M Na acetate and add enough solid Na acetate to bring to 1.0 M

Flow Rate: 0.55 ml/cm²/min

Column Washes: (1) 30 ml 0.3 M HNO₃, followed by 30 ml H₂O
 (2) 60 ml 0.5 M NaOH
 (3) 150 ml 0.5 M Na citrate pH 3 followed by 30 ml H₂O
 (4) 150 ml 0.1 M Na citrate pH 9 followed by 30 ml H₂O
 (5) 18 ml 6 N HCl

Elution of Ba product: 6 N HNO₃, 45 ml

Cation Eluted	% Lost in Sulfate Precipitation	% in Effluent+ Wash 1	% in Wash 2	% in Wash 3	% in Wash 4	% in Wash 5	% in Product	Material Balance
Sr	1.38	24.1	2.6	67.79	1.93	<0.01	<0.01	97.82
Ba	0.10	0.05	0.01	54.2	36.5	4.14	4.45	99.45

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Table IIISeparation of Fe, Cr, Ni, and Pb from Ba¹⁴⁰ by Ion Adsorption on Anion ExchangeResin

Conditions: Feed: 50 ml 0.5 M Na acetate containing:
 10 mg Fe⁺³; 10 mg Ba + Ba "tracer"; 10 mg Ni⁺²; 10 mg Cr⁺³
 50 mg Pb⁺² and 1.0 mg Sr⁺ "tracer"

pH: Runs I and II - 5.5
 Run III - 6.0

Anion Resin: Run I - 25 ml IR-4B
 Run II - 75 ml IR-4B
 Run III - 75 ml Dowex - A2

Activation: Resin initially in acetate⁻ form with Na acetate

Run No.	% In Effluent					
	Fe	Cr	Ni	Pb	Sr	Ba
I	25	62	3.7	3.5	-	-
II	2.4	18.8	1.1	5.0	105	88.6
III	<1.7	<2.6	<1.4	74	106	87.6

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FIGURE I
FLOWSHEET: PROPOSED RAILWAY EXCHANGE PROCESSES

Drawing # 7536

RESTRICTED DATA
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CAUTION
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PRECIPITATION PRODUCT:
100 gms Pb as PbSO₄
1 gm Ba as BaSO₄

Impurities:
Fe, Ni, Cr, and Sr

METATHESIS PRODUCT:
Pb⁺²
Ba⁺²
In dilute HNO₃

PROCESS I:
Dissolve in 6 N NaOH (CO₃ - Free); Dilute to 0.6 N NaOH
Volume = 20 Liters

PROCESS Ia:
Make 0.5 M in NaOH (CO₃ - Free)
Volume = 20 Liters

PROCESS II:
Dissolve in 1.0 M Na acetate
Volume = 20 Liters

PROCESS IIa:
Make 0.5 in Na acetate
Volume = 5 Liters

CENTRIFUGE:
Remove Fe, Cr, and Ni As hydrous oxides

STEP I A
WASH:
0.5 M NaOH (CO₃ - Free)
Vol. = 5 Liters

STEP I B
WASH:
0.5MNa citrate pH 3
Vol = 8-10 Liters

STEP II
WASH:
0.1MNa citrate pH 9
Vol = 6-10 Liters

STEP II I
WASH:
6 N HCl
Ca. 2 Liters

STEP IV
ELUTING AGENT
6 N HNO₃
1.5-2.0 Liters

STEP I
Both Processes
(For Processes II and IIa, only)
DOWEX-50
Column Diameter = 3 inches
Volume (total) = 600 to 1000 ml initially in Na⁺ Form

STEP II
WASH:
0.1MNa citrate pH 9
Vol = 6-10 Liters

STEP II I
WASH:
6 N HCl
Ca. 2 Liters

WASTE:
Pb as PbO₂: 99.99%
Fe: 60-90%
Cr: 50-100%
Ni: 3%

Fe
Pb

Sr: 99%
Na

PRODUCT:
Ba 99%
Sr 0.2%
Pb 0.01%
Fe, Ni, Cr: trace
Na/Ba = 0.08

* Under 10 (CO₃ - Free) atmosphere.

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81

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Drawing # 7534

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EUGENE DIETZEN CO.
MADE IN U.S.A.

NO 3410-10 DIETZEN GRAPH PAPER
10 X 10 PER INCH

Figure II

Elution of Ba With 2N HNO_3 , 6N HNO_3 And 6N HCl

Conditions: Resin: 10 ml Dowex-50, 140-200 mesh, initially in H^+ form, 1 column Volume = 6 ml
Flow Rate: 0.55 ml/cm²/min.

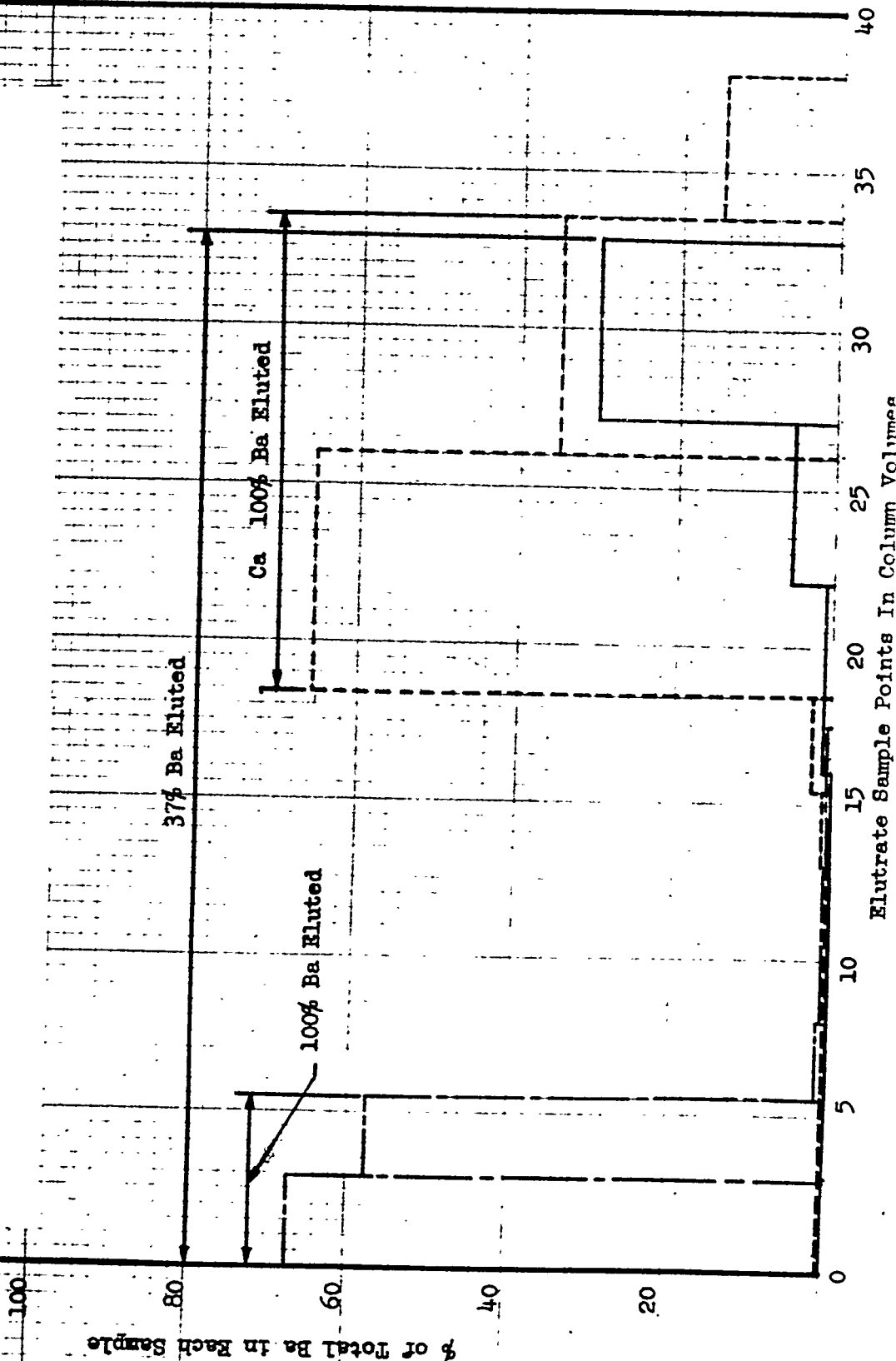
Feed: 10 mg Ba + Ba "Tracer"; Total vol. = 10 ml

Eluting Agent: Run Ba-23-2N HNO_3

Run Ba-24-6N HNO_3

Run Ba-25-6N HCl

% of Total Ba in Each Sample



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Drawing # 7535

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42

Figure 11

Na⁺ Capacity of IRC-"50" Resin as a Function of pH

Conditions:

Column: 5 ml (dry) IRC-"50" resin in H⁺ form

Activation:

(1) Down-flow - 25 ml 1.0M HCl; 10 ml H₂O

(2) Up-flow - 1.0M NaOH until effluent is alkaline + 20 ml excess

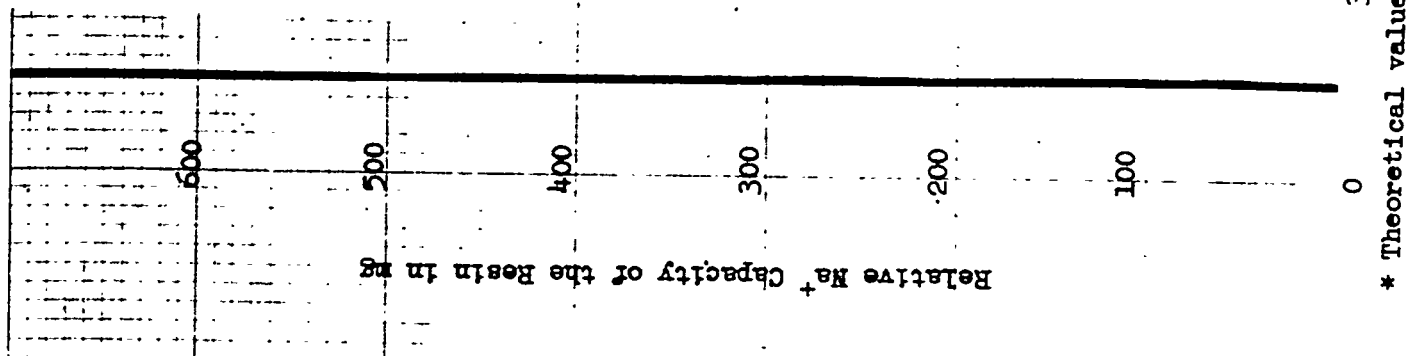
(3) Down-flow - 50 ml H₂O

Wash (Down-flow): (1) 1.0M Na acetate buffer solution until effluent equals feed pH

(2) 50 ml H₂O

Na Elution: 20 ml 1.0M HCl

Product: Take to dryness at 110°C and weigh as NaCl



* Theoretical value obtained from literature

~~SECRET~~

To: F. L. Steahly

Date: September 8, 1949

From: R. E. Blanco

Report Period: Aug. 10-Sept. 10

Distribution:

FLS

WKE

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WEU

Problem No. TDSI-30

Part 1

M O N T H L Y R E P O R T

This document consists of 2
pages and 0 figures.
No. 1 of 7 copies, Series a

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey, G. C. Blalock

Secret Notebook No. CL-2041

DECLASSIFIED

By Authority of:

AEC 4-19-61

M. J. H. H. H.

Mr. E. L. H. H.

Following Sample 2-21

OK

SUMMARY

The Acetate-Citrate Process for recovery and purification of Ba¹⁴⁰ by ion exchange is being pilot planted in the semi-works at present. Laboratory development work to improve this process is proceeding under the following headings:

Impurity Removal by Anion Exchange- Preliminary results reported in the quarterly report ending Aug. 10, 1949 showed that approximately 99% of the iron, chromium, nickel, and lead present in the RaLa process could be removed by making the solution 1.0M in sodium acetate, pH 5.5 to 6.0, and passing through an A2 or IR4B anion resin column. The results from 5 recheck runs using IR4B resin show the impurity removal to be no better than 80 to 90% with barium yields ranging from 15% to 85%. The rechecks on A2 resin showed even lower impurity removal. Since every effort was made to duplicate the conditions of the earlier runs, the conclusion reached is that in these runs an abnormal phenomenon such as colloidal physical adsorption or filtration of precipitated impurities must have taken place.

OPY

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Impurity removal by anion exchange will be abandoned for the present as adequate removal is being obtained in the cation exchange process.

Dowex 50 Resin v.s. IRC50 Resin for Separation of Barium and Strantium

In an effort to determine the optimum conditions for separation of barium and strontium, a large number of distribution coefficients have been run in the systems sodium citrate - Dowex 50 and sodium citrate - IRC-50. Determinations were made at 0.1, 0.3, and 0.5M sodium citrate and at pH's of 6.0, 7.8, and 9.0, as some of the analyses are being rechecked the results will be reported next month.

Comparison of Nalcite and Dowex 50

The distribution coefficients were determined for thorium and strontium Sr between the newer Dowex 50 type resin, Nalcite, and Dowex 50 and 0.5M sodium citrate at pH 9.0. The barium D.C.'s were 2.75 and 1.97 respectively while the strontium D.C.'s were 0.52 and 0.92. Thus the separation factor for barium and strontium using Nalcite is 5.28 while that for Dowex 50 is 2.14. The capacity of the air dry H forms of the two resins was 4.15 meq/gm for Dowex 50 and 4.37 meq/gm for Nalcite.

Investigation of Versene

Versene (ethylene di-amine-tetra-acetic acid) is a strong complexing (chelation) agent. The complexes are so strong that such compounds as barium and lead sulfate are easily dissolved. As the system is very dependent on pH, it is proposed to adjust the pH of the solution to the point where the Ba and Pb sulfates will not precipitate but where the Ba will be adsorbed on the resin and thus separated from the sulfate.

[REDACTED] COPY

49-11-361

85

FIS-181

Technical Division
Chemical Technology Department

To: F. L. Steahly

Date: November 8, 1949

From: R. E. Blanco

Report Period: Quarter Ending
Nov. 10, 1949

Distribution:

- (1) FLSteahly
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- (3) REBlanco
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Problem No. TDSI-30

Part

This document consists of 3
pages and 0 figures.
No. 1 7 Series NC

Q U A R T E R L Y R E P O R T

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey, G. C. Blalock

Secret Notebook No. 205, C1 2041

S U M M A R Y

The flowsheet of the Acetate-Citrate Process for recovery and purification of Ba¹⁴⁰ by ion exchange was presented in the quarterly report ending August 10, 1949. In this process the dilute nitric acid solution after metathesis is made 0.5 M in sodium acetate and passed through a Dowex 50 resin column where the Ba¹⁴⁰ is adsorbed. After removal of the impurities (lead, iron, strontium, etc) by selective elution the Ba¹⁴⁰ is recovered in 6 M nitric acid. Three laboratory demonstration runs on 1/30 plant scale showed that the barium loss would not exceed 2% and that impurities would not exceed 30% of the maximum tolerance. (See table I).

Development work to improve this process is proceeding as follows:

- (1) Versene v.s. Acetate

Versene (ethylene-diamine-tetra- acetic acid), a water soluble chelation agent, has been evaluated as a substitute for acetate in the feed solution at pH 6.0. The advantage gained is that the impurities (iron, lead,

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By Authority Of:
AEC 4-19-61
M. Shiley
Gen. L. E. B. Department

chromium and nickel) are complexed so strongly that no appreciable quantities are adsorbed on the resin with the barium. Thus the use of sodium hydroxide and pH 3 sodium citrate for lead and iron removal are eliminated, resulting in a $1/3$ reduction in time cycle. In addition, the barium-strontium separation ^{is} improved as the number of plates in the column was increased from 12 to 45. (Calculated from position and shape of elution curves). See Table I.

Versene, pH 6.5, has also been used to dissolve the lead-barium sulfate precipitate, thus eliminating the methathesis step. As the barium distribution coefficient is less favorable at this pH; 3 to 4 times as much resin is necessary to adsorb the barium as in the acetate-citrate process.

(2) Impurity Removal by Anion Exchange

A series of runs has shown that 80 to 90% of the iron, nickel, chromium, and lead impurities can be removed by passing the acetate solution through a column of IR-4B anion exchanger at pH 6.0. The barium yields are poor, however, ranging from 15 to 85%.

Two ion exchange procedures are being considered for the separation of barium from the uranium dissolver solution to replace the lead sulfate precipitation. The uranium can be complexed at pH 6.0-7.0 with "Versene" so that it may be possible to separate the barium from the uranium by ion exchange using IRC-50 resin thus making use of the preferential selectivity of this resin for the alkaline earths. A preferable complexing agent might be bicarbonate at higher pH's, since the capacity and selectivity of IRC-50 for alkaline earths has been shown to increase with pH. Consideration of the equilibria show that the $K_{s.p}$ of barium carbonate may not be exceeded under these conditions, however, its exact solubility will be determined. "Versene" might possibly be used to complex and dissolve the uranium in the Hanford waste tanks at a pH of approximately 7. The "Versene" could easily be recovered for recycle by acidifying and filtering off the precipitated "Versene".

Discussion: Month Ending November 10, 1949

The major effort has been divided into two projects:

(1) Three demonstration runs to show the reproducibility of the Acetate-Citrate Process on 1/30 plant scale.

(2) Improvement of the Acetate-Citrate Process by substitution of Versene (pH 6.0) for the acetate. (3 runs) Two runs were also made in which Versene at pH 6.5 was used to dissolve the lead-barium sulfate thus replacing the metathesis step presently used.

The following conclusions appear justified although all of the analyses are not completed as yet.

(1) The barium losses in the Acetate-Citrate Process will not exceed 2% and will probably decrease with increase in accuracy in analysis. Impurities in the product (i.e. iron, lead, etc.) will be less than 30% of the maximum tolerance.

(2) The advantage gained by use of Versene pH 6.0, instead of acetate is that the impurities (iron, lead, chromium, and nickel) are complexed very strongly and no appreciable quantities are caught on the resin with the Ba. Thus the use of sodium hydroxide and sodium citrate pH 3 for lead and iron removal are eliminated, resulting in a 1/3 reduction in time cycle. In addition, the barium-strontium separation is improved as the number of plates available for separation is increased from approximately 12 to 43 (calculated from the position and shape of strontium elution curve). Due to cross contamination in analyses the % strontium in the product in run 32 is no lower than in run 31. See Table I.

The results of a run in which Versene at pH 6.5 was used to dissolve the sulfate precipitate prior to adsorption^{on} a resin column showed the barium losses to be of the order of 4%. This loss can be lowered by use of more resin. A major disadvantage of this procedure is that the volume of resin used will be approximately 3 times that used for the other processes. This follows from the

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fact that more Versene and a higher pH must be used in order to hold the sulfates in solution resulting in a less favorable barium distribution coefficient.

A major disadvantage of all versene-cation exchange processes is the adjustment of the pH of a hot solution. ~~A scouting run~~ has been made using the anion exchange resin A2 and Versene in which it was not necessary to adjust the pH. The sulfate precipitate was dissolved in Versene with excess NaOH (pH approximately 11), and passed through the anion resin column where the cations were adsorbed as the Versene complex. The barium was selectively removed with pH 6.5 sodium acetate with a yield of % containing % of the Sr.

TABLE I

Ba¹⁴⁰ Purification

Conditions: Column:

30 ml Dowex-"50" Resin (100 - 200 mesh) Bed Depth 7"

Resin initially in Na⁺ form, activated with conc. NaNO₃(a) In Runs Ba-32, 34 and 36: Na⁺ Resin Buffered with 1.0 M Na Acetate, pH 6.0Flow Rate: 0.55 ml/cm²/min.

Feed:

Vol. 233 ml:

2.824 gms BB

34.65 mg Ba

32.8 mg Fe

3.24 mg Sr

10.4 mg Cr

10.0 ml Ba-Sr "Tracer"

6.16 mg Ni

(a) Runs Ba-31, 33 and 35, 0.5 M in Na Acetate;

(b) Runs Ba-32, 34 and 36, contain 20.0 ml 0.732 M Versene; pH 6.0

Washes:

I: 0.5 M NaOH

II: 0.5 M Na Citrate, pH 3

III: 0.1 M Na Citrate, pH 9

IV: 6 M H₂SO₄

Ba Elution:

6 M HNO₃(Note: Feed effluent and all washes flushed out of Resin Bed with H₂O)

Run No.	Waste Analyses (%)										Product Analysis (%)						Na Material Balance (%)	
	Effluent			Na Citrate, pH 9							HNO ₃							
	Ba	Fe	Pb	Ba	Pb	Ba	Fe	Ba	Sr	ml used	Ba	Ba	Sr	Fe	Pb	Ni, Cr		Ratio Na/Ba
Ba-31	0.5	92	6.3	0.44	2.7	0.1	3.6	ca 0.5	103	48	0.4	96	0.14	7	<0.02	7	1.14	97.6
Ba-33	0.02	122		0.005		0.012	7	0.082	91	48	0.008	106	*56	1.52		7	<0.04	121.1
Ba-35	0.03			0.004		0.042		1.45	34	75	0.013	102.4	0.67				—	104.3
Ba-32	0.29	91	—	0.04	—	0.67	7	0.54	108.7	48	0.08	110	0.04	7		7	1.59	112.3
Ba-34	0.1			0.35		0.08	ca 5.0	0.097	1.3	48	0.033	104.1	*76.2	7			<0.58	105.5
Ba-36	0.031			0.006		0.036		0.12	87.4	60	2.9	91	<0.17				1.69	94.1

* Poor separation of Ba and Sr was obtained when insufficient pH 9 Na Citrate was used as a result of recorded break-down

7 Not detectable by colorimetric analysis.

FLS-202

Technical Division

Chemical Technology Department

To: F. L. Steahly

Date: December 8, 1949

From: R. E. Blanco

Report Period: December 10, 1949

Distribution:

1. FLS
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Problem No. TDSI-30

Part 1

M O N T H L Y R E P O R T

This report contains 3 pages and 1 figure.
No. 1 of 7 copies, Series MC

Title: Purification of Ba¹⁴⁰ by Ion ExchangeWork by: R. E. Blanco, A. H. Kibbey, G. C. BlalockSecret Notebook No. 205SUMMARY

Development work on processes for the production of Ba¹⁴⁰ by ion exchange is proceeding under the following headings.

Improvement and Evaluation of the Acetate-Citrate Process

- (1) A run on 1/30 full chemical scale showed that if the iron in the starting solution is increased to ten times the maximum amount ever found in an actual run to date, the amount found in the product was still not detectible by spectrophotometric analysis.
- (2) Hydrochloric acid will be used to selectively elute sodium instead of sulfuric acid so that there will be no possibility of contaminating the product with sulfate.

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By Authority Of:

AEC 4-1961 (continued on next page)

For: H. T. Bray, Supervisor

~~SECRET DRAFT COPY~~

Versene* Process

This process is designed to replace the metathesis and the Acetate-Citrate Process by a two column ion exchange process employing Versene as the complexing agent. Incomplete results from 2 laboratory development runs on 1/36 scale indicate that the results will at least equal the former process. In addition the Versene process will reduce the total time cycle by an estimated 20 hrs.

The steps in this process are as follows:

- (1) Dissolve the barium and lead sulfate cake in 0.1 M Versene at pH 6.0 - 6.5 and pass through a Dowex 50 resin column where the barium is adsorbed while all of the sulfate and the bulk of the impurities (lead, iron, etc.) pass through.
- (2) The barium is eluted in a small volume of 0.3 M Versene pH 11, the pH adjusted to 4.0 - 4.5, and the barium readsorbed on a smaller column.
- (3) The strontium and any remaining iron, chromium and nickel are selectively eluted with pH 6.3, 0.07 M Versene and the sodium with hydrochloric acid.
- (4) The barium is eluted in 6 M nitric acid.

The variation of the distribution coefficients of barium and strontium with pH have been determined for synthetic Versene feed solutions v.s. Dowex 50 resin. The two solutions were 0.065 and 0.13 M in Versene and contained lead, iron, chromium and nickel but no sulfate. In the first case the amount of Versene was just enough to prevent the precipitation of the hydrous oxides. Thus the bulk of the Versene was complexed so that its effect on the barium and strontium was small. In the second case, however, the distribution coefficients decreased by factors greater than 100 as the pH changed from 5 to 7.

* Ethylene Di-amine tetra acetic acid.

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(See Figure 1).

Efforts to determine the distribution coefficients of the barium and strontium Versene complexes between a synthetic feed solution at pH 11 and the anion resin Dowex A2 were unsuccessful. The iron precipitated on contacting the hydroxyl form of the resin. The experiment will be rerun using the chloride resin form.

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Figure I

Drawing # 8123

Log Distribution Coefficients

KEUFFEL & ESSER CO., N. Y. NO. 548-1
Civil Engineering, 2 Cycle X 10 to the 100, 500 lines
Made in U.S.A.

0.01

100.0

0.1

2

3

4

5

6

7

8

9

1.0

2

3

4

5

6

7

8

9

10

2

3

4

5

6

7

8

9

10

2

3

4

Equilibrium pH

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Ba and Sr Distribution Coefficients
In A Versene Synthetic Feed System
As a Function of pH

Conditions:

Resin: "Dowex 50," 100-200 mesh,
sodium form buffered at
each pH with 0.5 M sodium
acetate, then water washed.

Aqueous phase:

Set I: 0.06M in Tetra sodium
Versene

Set II: 0.13M "

All Are: 1.0×10^{-3} M Ba
 1.0×10^{-3} M Sr
 5.9×10^{-2} M Pb
 2.7×10^{-2} M Fe
 8.5×10^{-4} M Cr
 4.3×10^{-4} M Ni

D.C. = $\frac{\text{cts/min/gm oven dry H}^+ \text{ Resin}}{\text{cts/min/ml solution}}$

Legend:

Set I:

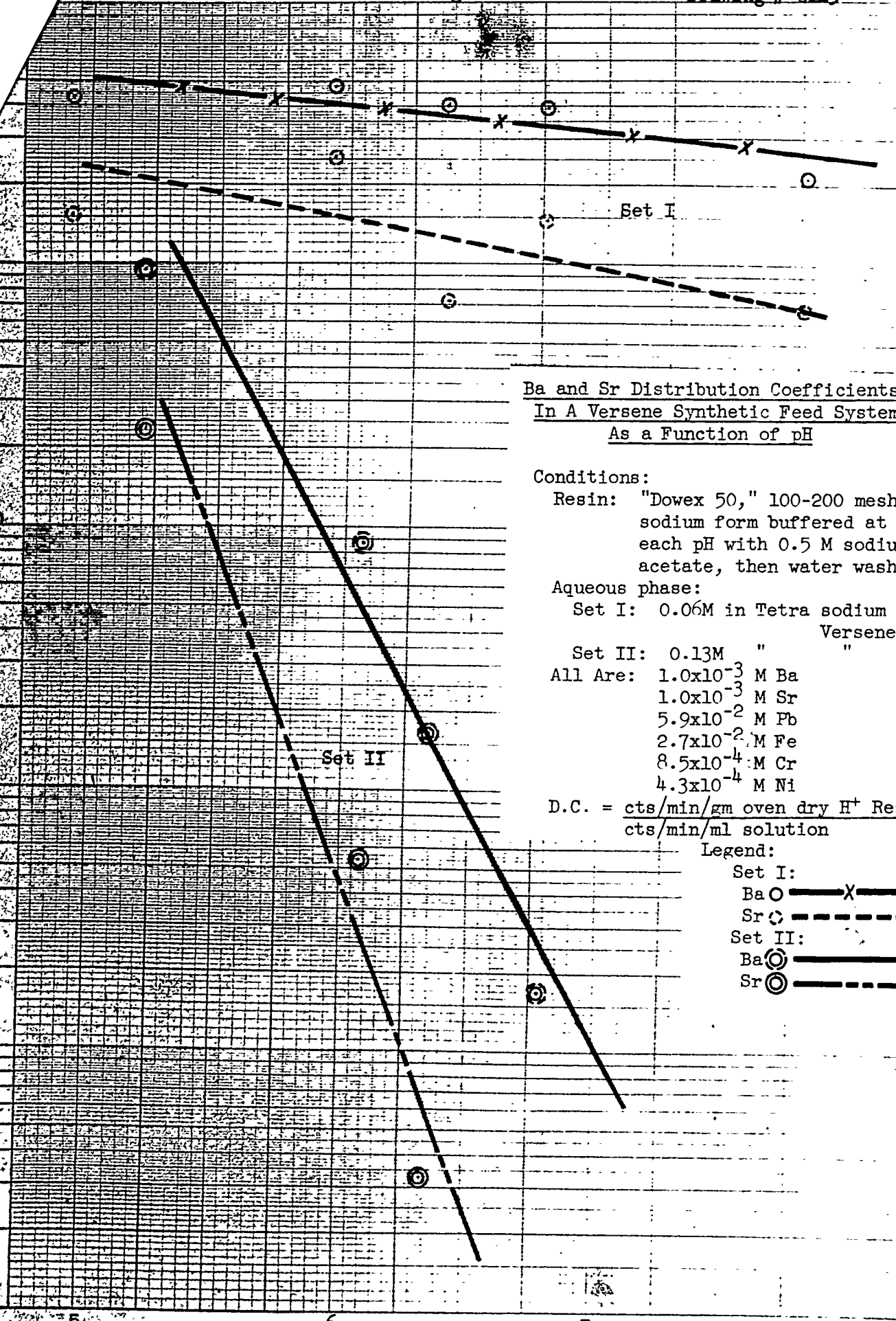
Ba \bigcirc ——— X ———

Sr \bigcirc - - - - -

Set II:

Ba \bigcirc ———

Sr \bigcirc - - - - -



50-1-200

72

FIS-225

Technical Division

Chemical Technology

Department

To: F. L. Steahly

Date: 1/9/50

From: R. E. Blanco *FE*

Report Period: 12/10/49-1/10/50

Distribution:

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7. FIS
8. WEC

Problem No. TDSI-30

This document consists of 9
pages and 6 figures.
No. 1 of 8 copies, Series FLS

Part 1

MONTHLY REPORT**DECLASSIFIED**

By Authority Of:

AEC 4-19-61M. Shiley

For: F. L. Steahly, Supervisor

Laboratory Control Dept.

SLS

Title: Purification of Ba¹⁴⁰ By Ion ExchangeWork by: R. E. Blanco, A. E. Hibbey, G. C. BlalockSecret Notebook No. 205 and C1 2041SUMMARY

Development work on processes for the production of Ba¹⁴⁰ by ion exchange is proceeding under the following headings:

* Versene Process:

In the Versene Process, which is being developed, the barium, strontium and lead sulfates are dissolved in 0.1 M Versene at pH 6.3 and run on an ~~M.S.~~ M.S. column of Na⁺ form Dowex - 50 resin, 50.8 cm. in height. Together with the sulfate, 50 to 90% of the strontium, and essentially all of the lead, iron, ^{nickle}nickel, chromium and rare earths pass through the column as their versenates (anion complexes), while the barium and the remainder of the strontium are adsorbed. The impure barium product is eluted in pH 11 Versene, the pH readjusted to 4.0 and the solution run on a 17.8 cm. high Purification Column of Na⁺-form Dowex-50 resin, on which the barium and traces of contaminants are adsorbed. Strontium and sodium are selectively eluted with 0.03M Versene, pH 6.3 and 0.5 M hydrochloric acid, respectively, leaving the barium on the column. The barium product is eluted in 6 N

*Ethylene-diamine-tetra-acetic acid.

**Metathesis substitute.

COPY

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nitric acid. Five laboratory runs on 1/36 full RaLa chemical scale have been completed. The results indicate that the product barium purity exceeds specifications and total barium loss is less than two percent. (See Table 1).

The Versene Process has several advantages over the Acetate-Citrate Process, namely: (1) elimination of the metathesis step used for the present process. This step has proved to be unreliable in process operations. (2) the overall time cycle required for the Versene Process is 10 to 15 hours shorter than that for the Acetate-Citrate Process, thereby reducing barium loss due to decay, and (3) Versene forms anion complexes with the bulk of the undesirable activities in the RaLa feed, allowing them to pass through the M.S. column in the feed effluent; a large amount of the activity is never caught on the column, thus reducing the probability of radiation decomposition of solutions and resin.

Improvement of the Acetate-Citrate Process:

In the Acetate-Citrate Process, strontium is separated from the barium by selective elution with 0.1 M sodium citrate at pH 9. In order to definitely establish optimum conditions of pH and sodium citrate molarity for the separation, the following investigations were made. Distribution coefficients and separation factors for barium and strontium were determined in the pH range from 6 to 9 for both IRC-50 and Dowex-50 resin-sodium citrate systems at citrate molarities of 0.1, 0.3 and 0.5 M. The separation factors for both systems were found to be almost independent of pH at constant citrate molarity. The influence of citrate molarity on the separation factor was shown by an increase of from 7 to 10 for the Dowex-50, and from 2 to 3 for the IRC-50, as the sodium citrate concentration was increased from 0.1 to 0.5 M at constant pH. As was expected from the equilibrium expressions, the distribution coefficients in the Dowex-50 system decreased slightly as the pH increased from

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from 6 to 9 at constant citrate molarity. However, in the IRC-50 system, an enormous increase in the distribution coefficient was noted when pH was increased from 6 to 9 -- approximating a factor of 50 when the citrate concentration was 0.1 M. The equilibrium equations for the system do not account for this marked increase, and a theoretical explanation will be offered in a separate report. Log plots of the barium and strontium distribution coefficients vs. equilibrium pH's for 0.1, 0.3 and 0.5 M citrate concentrations in both the IRC-50 and Dowex-50 systems are given in figures 1-6.

Slug Jacket Dissolving:

An effort has been made to find a method for slug jacket removal that will eliminate the objectionable siliceous material that bonds the aluminum can to the slug. This material plugs the filter. The success of such a method would eliminate the projected use of the dissolver crud filter. The procedure below, which appears very promising, was developed by using cold Clinton slugs, especially coated with the Al-Si-U alloy by the Metallurgical Department.

- (1) To remove the aluminum can, boil 2 hours in a ^{hydroxide solution which is 1.76 m in potash} 6.25 M sodium nitrate.

The nitrate serves to oxidize the hydrogen evolved, and so prevents explosion hazard.

- (2) Boil 5-1/2 hours in 6.25 M sodium hydroxide.

- (3) Boil 3 hours in 1.0 M nitric acid containing a trace of mercuric ion as a catalyst. In this final cleanup, the siliceous material is not dissolved, but rather, is undercut so as to allow its removal by flaking off. See table 2 for laboratory results. The time cycle for the proposed dissolving method is 10-1/2 hours, resulting in a 2 to 2-1/2% barium decay loss; uranium loss is below 1%. The addition of hydrogen peroxide to the 6.25 M sodium hydroxide appears to accelerate the reaction and is being investigated.

Adsorption Of The Sulfate And Metallic-Anion Complexes Present In A Synthetic ~~Versene~~ Feed:

An effort to replace the metathesis step in the present RaLa process by anion exchange has been made. However, the use of A2-resin for the removal of sulfate and barium and lead versenates from a synthetic-Versene feed solution of barium and lead sulfate has so far been unsuccessful. A large excess of Versene is required to prevent iron precipitation at high pH. Apparently this excess of strongly adsorbed tetravalent anion material saturates the anion resin, preventing adsorption of the more weakly held anion metallic complexes. Future experiments are being planned at lower pH values, where the concentration of Versene can be decreased.

Discussion:

*Versene Process:

A total of five laboratory runs, on 1/36 full RaLa chemical scale, have been completed that indicate that the two column Versene Process for the purification of Ba^{140} by ion exchange has decided advantages over the Acetate-Citrate Process: (1) the metathesis step currently used in RaLa, which has been found to be unpredictable, is eliminated; (2) the total process time is reduced by 10 to 15 hours, affording an increase in barium yield of approximately 2 to 3% due to the shorter decay period; (3) a greater portion of the undesirable activities in the feed, including 50 to 90% of the strontium and the bulk of the rare earths, pass through the ** M.S. column in the feed effluent as versene anion complexes, while the barium is adsorbed on the resin. With most of the strontium and rare earths passing through the bed, the concentration of high level activities in small areas does not occur to such a great extent, hence the probability of radiation damage to resin and

*Ethylene-diamine-tetra-acetic acid.

**Metathesis substitute.

solutions is decreased appreciably. It should also be noted that in the Versene Process total barium losses are less than 2% and the purity of the barium product exceeds specifications.

In the first laboratory runs, the Purification column employed was 7.6 cm. in height. However, since barium losses were large (3 to 5%) in the strontium and sodium elution steps, the column height was increased to 17.8 cm. in the last two runs. Also, in the last two runs, the strontium elution was carried out with 0.03 M Versene at pH 6.3 instead of 0.07 M as used in the first three runs; in addition, the normality of the hydrochloric acid for sodium elution was reduced to 0.5 N as compared with 6 N in the first three runs. By using less concentrated eluting agents in conjunction with a longer Purification Column, more efficient separations and smaller barium losses have been achieved.

Specifications for the M.S. and Purification Columns, together with feed conditions and results for all five runs are given in Table 1.

Improvement Of The Acetate-Citrate Process:

The effects of pH and sodium citrate molarity in the Acetate-Citrate Process have been investigated in an effort to find optimum conditions for maximum separation of barium and strontium. Distribution coefficients in both IRC-50 and Dowex-50 resin - sodium citrate systems have been determined in the pH range from 6 to 9 for 0.1, 0.3 and 0.5 M sodium citrate. It was observed that the barium and strontium separation factors in both resin systems were not particularly ~~KAREKKA~~ pH dependent. As citrate molarity was increased from 0.1 to 0.5 M, pH remaining constant, an increase in separation factor from 2 to 3 for the IRC-50, and from 7 to 10 for the Dowex-50 was noted. The barium and strontium distribution coefficients for the Dowex-50 system decreased slightly with an increase in pH-at constant citrate concentration, as was expected from the equilibrium formulae. For the IRC-50 system, however, the distribution

coefficients increased enormously as the pH was raised from 6 to 9 -- a factor of approximately 50 in the case of the 0.1 M sodium citrate. This great increase is not accounted for by the equilibrium expression and a discussion of the theory involved will be presented in a separate report. It is expected that this large increase in the barium distribution coefficient with increasing pH will prove advantageous in the separation of barium and uranium. Graphical representations of these distribution coefficient data are given in figure 1-6.

Slug Jacket Removal:

An effort has been made to dissolve the U-Al-Si alloy bonding agent, that holds the aluminum can on the slug, with a minimum barium and uranium loss. By eliminating the objectionable siliceous material that has caused plugging of the metathesis filter, the installation of a filter and use of filter aid in the line between the dissolver and metathesis tanks would be avoided. The conditions which appear to be most favorable for dissolution of the slug coating are as follows: (1) boil for 2 hours in a solution 6.25 M in sodium hydroxide and 1.76 M in sodium nitrate. The sodium hydroxide dissolves the aluminum can and the sodium nitrate oxidizes the hydrogen evolved, preventing explosion hazard; (2) boil an additional 5-1/2 hours in 6.25 M sodium hydroxide to complete dissolution of the can. Small areas of black coating still remain on the after this treatment; (3) boil for 3 hours in 1.0 M nitric acid containing a trace of mercuric ion as catalyst. This final cleanup step does not dissolve the siliceous material, but undercuts it so as to allow its removal by scaling off. The time cycle for this proposed method is 10-1/2 hours, as compared to 6 hours for the present method. However, by utilization of the new method, the slug coating is essentially completely removed, and any small particles of coating remaining on the slug are not sufficient to seriously hamper filtering operations. In the very near future, this method will be tried on actual Hanford slugs. With the new method, barium losses due to decay would be approximately 2 to 2-1/2% compared to 1% for the present process.

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-7-
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Uranium losses in both processes are less than 1%. (See Table 2). The addition of hydrogen peroxide to the 6.25 M sodium hydroxide solution appears to accelerate the reaction and the possibility of shortening the time cycle by its use is being investigated.

Adsorption Of The Sulfate And Anion-Metallic Complexes Present in A Synthetic Versene Feed:

An effort has been made toward replacing the metathesis step in the present RaLa process with an anion exchange column. However, the use of A₂- (anion) resin as an agent for the removal of the sulfate and barium and lead versenates from a versene feed solution, containing an amount of sulfate equivalent to the barium, strontium and lead, has been found to be ineffective. Synthetic feeds for the A₂-resin experiments were 0.001 M in barium and strontium, and contained a large excess of Versene (0.166 M), radio - active barium - strontium tracer, nickle, ~~chromium~~, iron and lead. A suitable aliquot of the feed was shaken for 24 hours with 20 to 23 ml of A₂-resin, and the supernate sampled for analysis. In the first run, the A₂-resin was initially in the hydroxyl form, and the high equilibrium pH, ca. 11, allowed the iron to precipitate as hydrous ferric oxide. In the next run, the chloride form of the resin was used, lowering the equilibrium pH to 9.2, and although no iron precipitated, only a negligible portion of the barium and lead was adsorbed on the resin. Presumably, the excess free Versene was adsorbed more strongly than the barium and lead versenates because of its tetravalence, occupying all of the available adsorption space, leaving little or none for the more weakly-held, divalent, barium and lead anion complexes. Some future experiments are being considered which will be made in the pH range from 6 to 7 since at these lower pH's, a much smaller excess of Versene is required to keep the cations from precipitating.

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TABLE I

VERSENE PROCESS FOR BA ¹⁴⁰ PURIFICATION

Conditions:

Columns: Resin (for all columns) - Dowex-50, 100-200 mesh, initially in Na⁺ form
 Dimensions: *M.S. Column - 50.8 cm. ~~dia.~~ x 1.7 cm. diam.
 Purification Column - Runs V-16, 17 and 18 - 7.6 cm. ~~dia.~~ x 1.7 cm. diam.
 Runs V-19 and 20 - 17.8 cm. ~~dia.~~ x 1.7 cm. diam.

Procedure:

*M. S. Column: Feed - 1/36 full RaLa scale Chemical under maximum conditions of impurity:

22.0 mg Fe
 29.7 mg Ba
 3.18 mg Sr
 Ba-Sr "tracer"

Volume = 200 ml, 0.10 M in Versene

pH: Run V-16, 6.0; Runs V-17, 19 and 20, 6.3; Run V-18, 6.5

Impure product - eluted in 0.25 M Versene, pH 11.2

Purification Column: Feed - Impure product from M.S. adjusted to pH 4.0 (final volume approximately 300 ml)

Eluting Agents - Sr elution (V-16, 17 and 18) - 0.07 M Versene, pH 6.3
 (V-19 and 20) - 0.03 M Versene, pH 6.3
 Na elution (V-16, 17 and 18) - 6 N HCl
 (V-19 and 20) - 0.5 N HCl
 Ba product - 6 N HNO₃

Run No.	* M. S. Column					Purification Column										Ba Material Balance															
	Waste Analysis (%)					Impure product (%)					Waste Analysis (%)						Product Analysis														
											Feed						pH 6.3					Versene					HCl				
											Ba	Sr	Fe	Pb	Ba		Ba	Sr	Fe	Ba	Ba	Sr	Fe	Ba	Ba	Sr	Fe	Ba	Ba	Sr	Fe
V-16	1.2	55	81.8	124.		0	0.3	26.8	4.6		108.2	0.7	108.2	0.05	#									0	109.7						
V-17	0	94.0	40.9	140.		0.04	1.07	22.5	5.08		75.4	3.17	75.4	0.06	#									0	98.7						
V-18	0.27	78.2	44.5	131.		3.1	2.4	8.3	13.9		81.4	54.7	81.4	0.06	#									0.11	100.01						
V-19	0.73	79.3	65.6	136.		0.6	0.78	17.9	1.8		96.1	0.76	96.1	0.2	#									12.	104.1						
V-20	1.	76.3				0.3	1.	18.4	1.		101.1	0.29	101.1		#									7.05							

*M.S. = Metathesis Substitute

† = Not detectable by spectrophotometric analysis

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Table 2

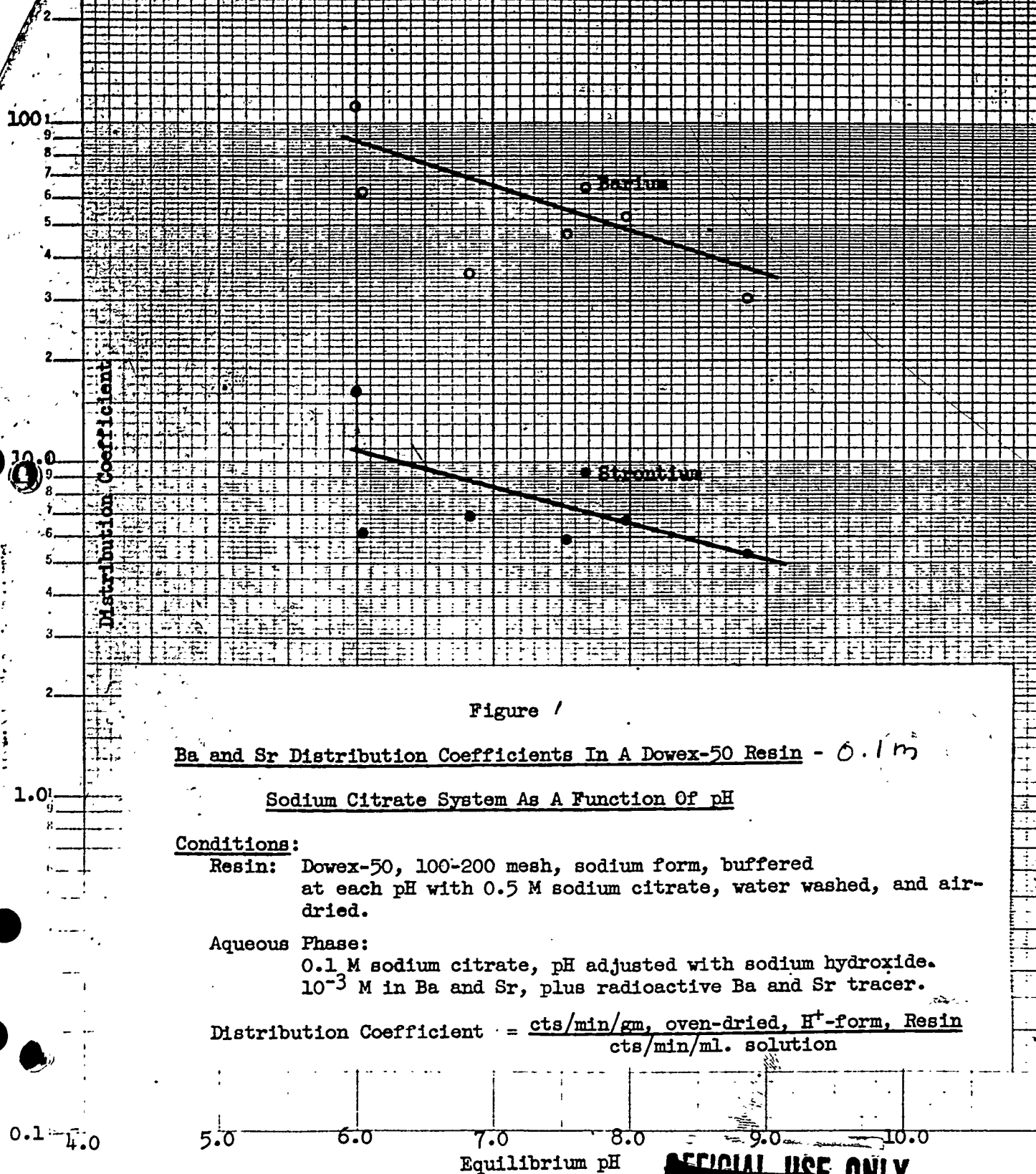
Slug Jacket RemovalConditions:

200 ml. of each reagent was used in each step.
 The 6.25 M NaOH solution was changed at approximately 4 hr. intervals.
 U losses were determined by analytical analysis of the nitric acid solutions.

Slug No.	Slug Treatment: (hours of boiling)			Step IV: 1.0M HNO ₃ + trace Hg ⁺²	Step V: 6.25M NaOH	Total Treat- ment Time (hrs.)	U Loss (%)	Remarks
	Step I: 6.25 M NaOH + 1.76 M NaNO ₃	Step II: HNO ₃ -H ₂ SO ₄ - H ₃ PO ₄ Mixture	Step III: 6.25M NaOH					
2	2	-	12-1/2	2	-	16-1/2	0.51	Slug quite clean only a few small patches of coating left.
3	4-1/2	3/4	-	-	-	5-1/4	ca. 15	Slug very clean but deeply pitted.
4	2	-	3 (H ₂ O ₂ Added)	2	2 (H ₂ O ₂ Added)	9	6.13	Slug very clean
*5	2	-	2-1/2	3	3	10-1/2	6.7	Only one very small spot of coating left.
6	-	-	16 + 32 (cold)	2-1/2	-	50-1/2	0.11	Slug clean and shiny.

*Proposed Method.

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Figure 2

Ba and Sr Distribution Coefficients In A Dowex - 50 Resin- 0.3 M

Sodium Citrate System As A Function Of pH

Conditions:

Resin: Dowex-50, 100-200 mesh; sodium form, buffered at each pH with 0.5 M sodium citrate, water washed, and air-dried.

Aqueous Phase:

0.3 M sodium citrate, pH adjusted with sodium hydroxide.
10⁻³ M in Ba and Sr, plus radioactive Ba and Sr tracer.

$$\text{Distribution Coefficient} = \frac{\text{cts/min/gm, oven-dried, H}^+\text{-form, Resin}}{\text{cts/min/ml solution}}$$

Distribution Coefficient

Barium

Strontium

Equilibrium pH

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not printed 4 (times X 10 to the left 5th line counted)

100

1.0

0.1

4.0

5.0

6.0

7.0

8.0

9.0

10.0

Figure 3

Ba and Sr Distribution Coefficients In An ^{Dowex-50} IRC-50-Resin- 0.5M

Sodium Citrate System As A Function Of pH

Conditions:

Resin: Dowex-50, 100-200 mesh; sodium form, buffered at each pH with 0.5 M sodium citrate, water washed, and air-dried.

Aqueous Phase:

0.5 M sodium citrate, pH adjusted with sodium hydroxide.
10⁻³ M in Ba and Sr, plus radioactive Ba and Sr tracer.

Distribution Coefficient = $\frac{\text{cts/min/gm, oven-dried, H}^+\text{-form, Resin}}{\text{cts/min/ml. solution}}$

Distribution Coefficient

Barium

Strontium

Equilibrium pH

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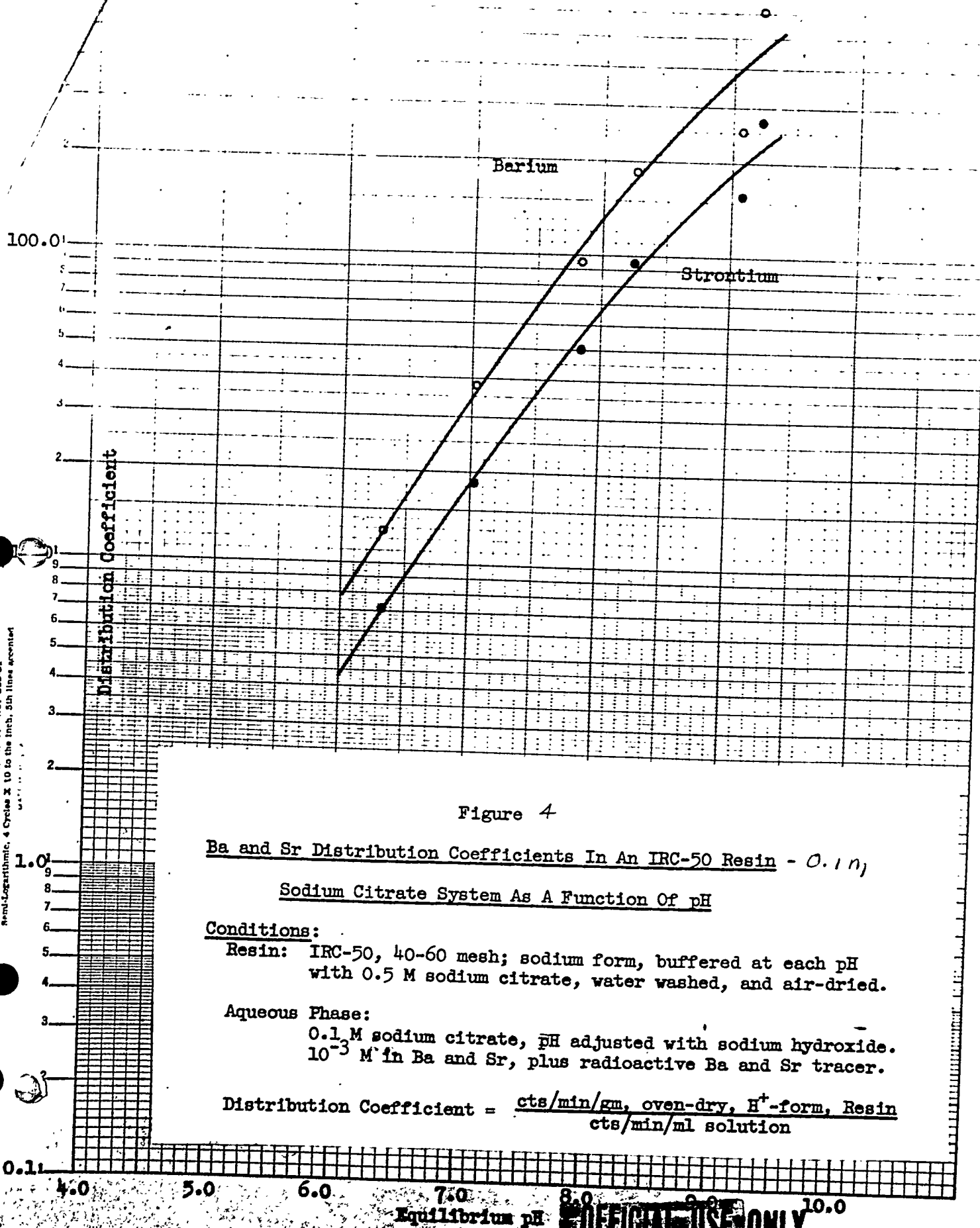


Figure 4

Ba and Sr Distribution Coefficients In An IRC-50 Resin - 0.1 n₁
Sodium Citrate System As A Function Of pH

Conditions:

Resin: IRC-50, 40-60 mesh; sodium form, buffered at each pH with 0.5 M sodium citrate, water washed, and air-dried.

Aqueous Phase:

0.1 M sodium citrate, pH adjusted with sodium hydroxide.
 10^{-3} M in Ba and Sr, plus radioactive Ba and Sr tracer.

Distribution Coefficient = $\frac{\text{cts/min/gm, oven-dry, H}^+\text{-form, Resin}}{\text{cts/min/ml solution}}$

Figure 5

Ba and Sr Distribution Coefficients In An IRC-50 Resin - 0.3m

Sodium Citrate System As A Function Of pH

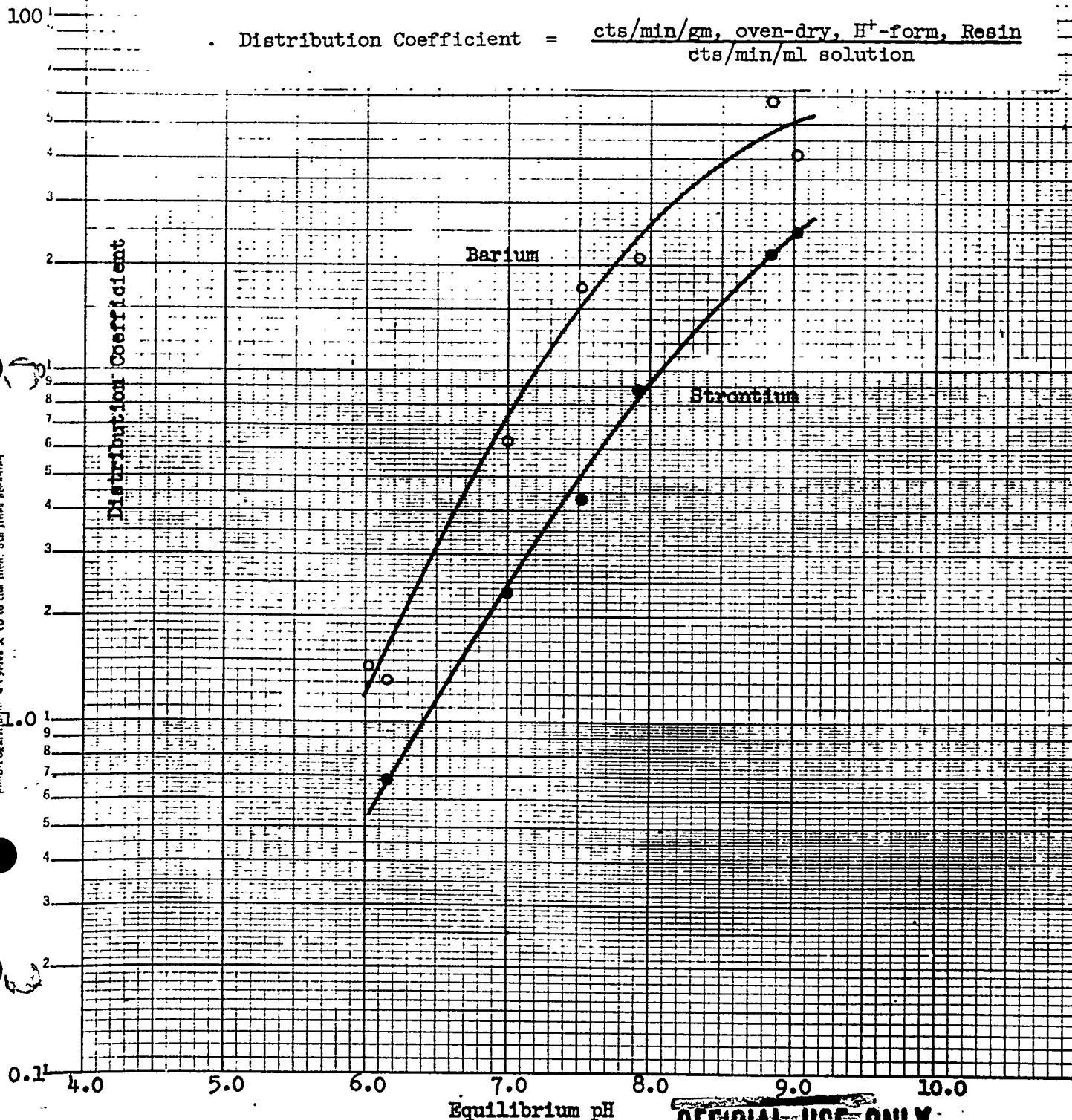
Conditions:

Resin: IRC-50, 40-60 mesh; sodium form, buffered at each pH with 0.5 M sodium citrate, water washed, and air-dried.

Aqueous Phase:

0.3 M sodium citrate, pH adjusted with sodium hydroxide.
10⁻³ M in Ba and Sr, plus radioactive Ba and Sr tracer.

$$\text{Distribution Coefficient} = \frac{\text{cts/min/gm, oven-dry, H}^+\text{-form, Resin}}{\text{cts/min/ml solution}}$$



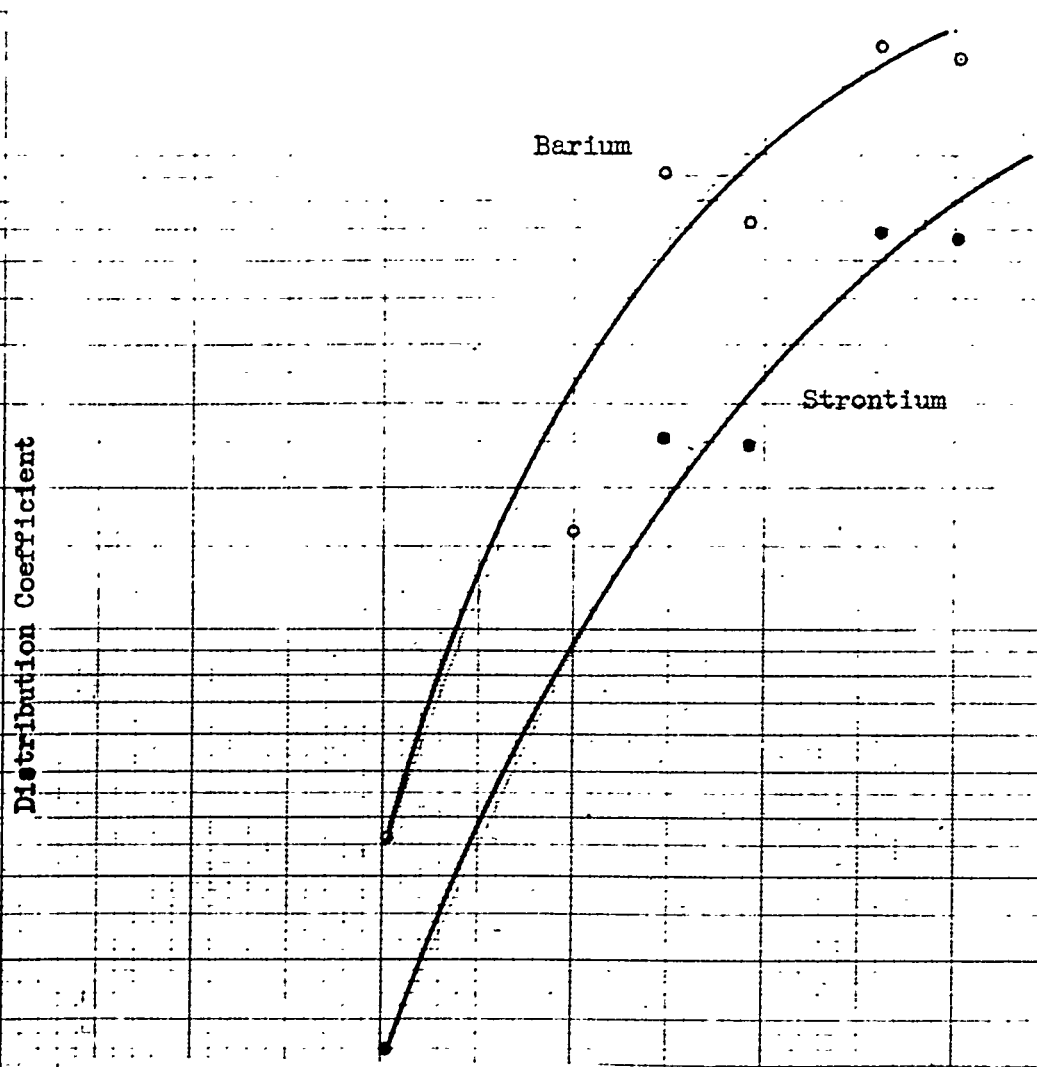


Figure 6

Ba and Sr Distribution Coefficients In An IRC-50 Resin- 0.5 M,
Sodium Citrate System As A Function Of pH

Conditions:

Resin: IRC-50, 40-60 mesh; sodium form, buffered at each pH with 0.5 M sodium citrate, water washed, and air-dried.

Aqueous Phase:

0.5 M sodium citrate, pH adjusted with sodium hydroxide.
 10^{-3} M in Ba and Sr, plus radioactive Ba and Sr tracer.

Distribution Coefficient = $\frac{\text{cts/min/gm, oven-dry, H}^+\text{-form, Resin}}{\text{cts/min/ml solution}}$

Equilibrium pH

To: F. L. Steahly

Date: February 10, 1950

From: R. E. Blanco

Report Period: Month ending Feb.
10, 1950

Distribution:

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Part

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No. 1 of 2 copies. Series MCMONTHLY REPORT**DECLASSIFIED**

By Authority Of:

E. J. Murphy 5-25-60
MTFor: H. I. Gray, Supervisor
Laboratory Records Dept.
CJHTitle: Purification of Ba¹⁴⁰ by Ion ExchangeWork by: R. E. Blanco, A. H. Kibbey, G. C. BlalockSecret Notebook No.SUMMARY

Work is continuing on the development of an ion exchange process for the purification of radio barium. Laboratory development of two processes, the Acetate-Citrate process and the two column Versene process, has been completed. These processes showed reproducibility, a product yield of the order of 98%, and a product purity which met or exceeded specifications. Flowsheets for these processes were presented in the monthly report ending January 10, 1950. and the quarterly report ending Nov. 10, 1949.

A new less stringent specification for the amount of radio strontium that can be present in the product, permits the use of a sampler one column Versene process. The steps in this process are:

- (1) Dissolve the barium-lead sulfate cake in 0.14 M Versene* and adjust the pH to 6.0 - 6.5.
- (2) Pass the solution through the resin column where the barium is adsorbed while the bulk of the impurities, iron, lead, strontium, rare earths, chromium, and nickel pass through.
- (3) Elute any adsorbed impurities by washing the column with pH 6.3, 0.07 M Versene.

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- (4) Elute the sodium with 1 M hydrochloric acid.
- (5) Elute the pure barium in 6 M nitric acid.

The yield of barium in the 1st trial run of this process was greater than 95%.

Impurity removal was more than adequate except for iron which was marginal. The problem of iron removal will be attacked by the use of a new reagent, Fe 3 Specific, * in the feed solution. This compound complexes iron and other heavy metals but not alkaline earths.

In order to avoid a pH determination on the hot feed, the effect of acetate buffer on the system was studied. It was shown that if the Versene solution is made 0.5 M in sodium acetate and adjusted to pH 7.7, prior to its addition to the barium-lead sulfate cake, the final pH of the solution will fall in the desired range, 6.0-6.5, even though the amount of lead may vary by 20%. A run using such a feed showed a 15% barium loss, however. Further development is necessary.

Hanford Slug Jacket Removal

Laboratory work in this project is essentially complete. The 12 hour procedure as follows gave excellent results.

- (1) Boil 2 hours in a solution 6 M in caustic and 1.7 M in sodium nitrate.
- (2) Boil 7 hours in a fresh solution of 6 M caustic.
- (3) Boil 3 hours in 1M nitric acid.

The uranium loss was less than 1%. One section of slug required an additional caustic and nitric acid treatment. Several runs will be made on separate slugs to check the uniformity of the siliceous alloy.

*Di ethanol glycine

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FLS-272
Chemical Technology Division

To: F. L. Steahly

Date:

From: R. E. Blanco *REB*

Report Period: Ending 3-10-50

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No. 1 of 2 copies, Series FLS

By Authority Of:

E. J. Murphy 5-25-60
gmH

For: M. T. Bray, Supervisor
Laboratory Records Dept.
ORNL

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey, G. C. Blalock

Secret Notebook No. 205, 249

SUMMARY

Work is continuing on the development of a one column Versene ion exchange process for the purification of radio barium.

The steps in the process are:

- (1) Dissolve the barium-lead sulfate cake in 0.14 M Versene and adjust the pH to 6.0 - 6.5.
- (2) Pass the solution through the resin column where the barium is adsorbed while the bulk of the impurities, iron, lead, strontium, rare earths, chromium, and nickel pass through.
- (3) Elute any adsorbed impurities by washing the column with 0.07 M, pH 6.3, Versene.
- (4) Elute the sodium with 1 M hydrochloric acid.
- (5) Elute the pure barium in 6 M nitric acid.

The yield of barium is greater than 95% with adequate purity.

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Investigation of Process Variables

Column Dimensions

Trial runs were made on columns 10", 15" and 18" in height. The results show that the column must be at least 18" high to obtain a high product yield. For safety on full chemical scale the column bed should measure 20" X 3" when the resin is in the sodium form.

Iron Removal

The amount of iron left in the product ^{just}~~first~~ meets specifications. Since it is desirable to have a safety factor, the use of Fe (3) specific*, an iron complexing agent, was investigated as a feed constituent. A series of distribution coefficients for iron, barium, and strontium between 0.05, and 0.1 M Fe (3) specific solution and Dowex 50 resin were run in the pH range 5.0 to 8.0. The results showed that the iron distribution coefficients were very low so that essentially no iron was adsorbed on the resin in this pH range. The barium and strontium distribution coefficients, however, were very high and decreased as the pH increased.

The use of 0.1 M Fe (3) specific in a Versene feed solution resulted in a 15% barium loss. The use of 0.01-0.05 M specific should be adequate. It was found that 13% less Versene was needed to dissolve the barium-lead sulfate cake when the solution was 0.1 M in Fe (3) specific.

An ^{ALICHOOT}~~aliquot~~ of fresh resin was cleaned thoroughly with nitric acid, ashed, and the residue analyzed for iron. The results showed that 34 ml of resin as received from the manufacturer contains about 1 mg of iron in its structure.

Elution of Impurities

Iron and chromium were found to be ~~XXXX~~ ^{ir}reversible in the resin - Versene system. That is, when initially complexed by the Versene iron and chromium ^{one}~~one~~ not appreciably adsorbed on the resin. However, their elution from the resin

* N-di-ethanol-gly~~col~~

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with Versene is inefficient. Fe (3) specific elutes iron quite readily while lead and nickel are easily eluted with Versene.

Elimination of Organic Color From the Product

The product will undoubtedly contain a small amount of colored organic material as a result of the decomposition of the resin by radiation. Experiments on synthetic color, produced by the action of ^{conc.} ~~con.~~ nitric acid and peroxide on resin, show that the color can be eliminated by the use of 30% peroxide or aqua regia. However these processes are undesirable as the former forms insoluble barium oxides and the later presents corrosion problems. The use of ozone or precipitation of the barium in 18 M nitric acid is being considered. The precipitation would avoid the evaporation step and offer additional impurity decontamination.

Sodium Acetate As a Feed Buffer

Sodium acetate was considered as a feed buffering agent so that the determination the pH of the "hot" feed would be eliminated. Treat runs, using Versene feeds 0.5 M in sodium acetate, showed that the column size would have to be more than doubled in order to achieve adequate barium yields so that a Versene Acetate feed is considered impractical at present.

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FLS-332
Chemical Technology Division
Laboratory Section

To: F. L. Steahly

From: R. E. Blanco

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Problem No. TDSI-15

Part

QUARTERLY REPORT

DECLASSIFIED

By Authority Of:

E. J. Murphy 5-25-60
JMH

For: H. T. Bray, Supervisor
Laboratory Records Dept.
ORNL

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibby, G. C. Blalock

Secret Notebook No.

SUMMARY

I. Development of a One Column Versene Process

Development of a one column Versene process for the production of radio barium on a 3000 curie level has been completed. This process eliminates the metathesis step by dissolution of the sulfate cake in Versene. Barium yields are at least 95% and are of adequate purity. The process steps were outlined in the report ending March 10, 1950.

This process is not suitable, however, for production of 10,000 curies where the amounts of barium and strontium are much larger. The large amount of Versene required to dissolve a 10,000 curie sulfate cake necessitated the use of a resin column of unreasonable height for adsorbing the barium. For production of 10,000 curies it is recommended that the bulk of the sulfate be removed by metathesis with potassium carbonate prior to the Versene

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(continued)

process. Experiments, in which the solubility of barium, strontium and lead sulfates in Versene as a function of Versene concentration, pH, and sulfate concentration were determined, showed that the metathesis should be approximately 99% complete to insure complete dissolution of the sulfate cake.

A new system is under investigation in an effort to eliminate metathesis and still retain a reasonable resin column height. In this system the Versene feed is passed through a nickel form resin bed. Since the nickel-versene complex is much stronger than the versene complexes of barium and strontium, the nickel is preferentially complexed, leaving barium and strontium free to adsorb on the resin. Laboratory runs are being made for determination of critical column dimensions, pH ranges and nickel concentrations.

II. Elimination of Organic Color in the Product

It is possible that organic color will be present in the product solution as the result of resin decomposition by radiation. If necessary, these objectionable organic contaminants can be eliminated by evaporation of the product solution to 2 liters (70% nitric acid) and addition of an equal volume of 98% fuming nitric acid, bringing the solution to 85% nitrate. By filtration, the soluble organic material is separated from the barium nitrate precipitate, which is then dissolved in water. The barium obtained by this method, using a synthetic product solution colored with resin decomposition products, was free from organic color. The barium loss was 0.25%. Aqua regia or 30% hydrogen peroxide were effective in destroying the color, but the former presents corrosion problems and the latter forms insoluble

~~_____~~
~~_____~~
~~_____~~
~~_____~~
~~_____~~

(continued)

oxides of barium. Results obtained with ozone were negligible.

III. Sodium Acetate as a Feed Buffer

Sodium acetate was considered as a feed buffering agent in an effort to eliminate the adjustment of pH on the "hot" feed. Test runs using Versene feeds 0.5 M in sodium acetate indicated that the column size would have to be more than doubled in order to achieve adequate barium yields, therefore a Versene Acetate feed is considered impractical at present.

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58-4-197 114

FIS-296
Chemical Technology Division

To: F. L. Steahly

Date:

From: R. E. Blanco *RS*

Report Period: Month Ending April 10, 1950

Distribution:

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Problem No. TDSI-5

This document consists of 2 pages and 0 figures
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Part

MONTHLY REPORT

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. ~~Kimsey~~ *G. C. Blalock*

~~SECRET~~

Authority Of:

G. Murphy 5-25-60
D. McKelvie

Secret Notebook No. 205

For: H. I. Gray, Supervisor
Laboratory Records Dept.
ORNL

SUMMARY

I. Development of a One Column Versene Process

Development of a one column Versene process for the production of 3000 to 5000 Curies of radio barium has been completed. This process, the steps of which were outlined in the monthly report ending March 10, 1950, produces product of adequate purity and in yields greater than 95%.

It was found that this process will need further development when applied to the production of 10,000 curies since the amount of barium and strontium will be increased to approximately 2 gms. each. A much higher concentration of Versene will be needed in the feed to hold the sulfates in solution, which in turn, will necessitate a larger resin column. Preliminary experiments showed that only a 20% yield was obtained when the column size was 36" x 4".

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-2-

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2.0 Elimination of Organic Color in the Product

It is possible that organic color will be present in the product solution as the result of resin decomposition by radiation.

Consumer evaluation of a hot run will be necessary to settle the question of the amount of organic and its harmful qualities. The following method for elimination of the organic material has been developed in case this procedure is necessary.

- (1) Instead of evaporating the product solution (5 liter of 6 M nitric acid) to dryness, it is evaporated to 2 liters.
- (2) 2 liters of 98% fuming nitric acid are added, bringing the solution to 85% nitrate. The solution is filtered and the precipitated barium nitrate retained on the filter while the organic color passes through in the solution.
- (3) The precipitate is dissolved in water and drawn through the filter for final evaporation in the shipping can.

This process was tried and the results show that when as much as 5 gms. of dissolved resin were present, the barium loss was only 0.25% and the product was free from colored organic material.

A demonstration of this procedure, in which the original product solution was evaporated to 100 ml instead of 2 liters, resulted in a 50% product loss, probably as barium sulfate.

A separate experiment, which might account for the difference in the two procedures, showed that at least 20% of the BaSO_4 can be metathesized to $\text{Ba}(\text{NO}_3)_2$ with 85% fuming nitric acid.

Ozone was tried in an effort to ^{destroy}~~destroy~~ the organic color but produced negligible results.

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FIS-374

Chemical Technology Division

50-6-225 119

To: F. L. Steahly

Date: Month Ending June 10, 1950

From: R. E. Blanco

Report Period:

Distribution:

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2. WKE
3. RMB
4. FRB
5. JOD
6. DGR
7. FLC

Problem No. TDSI-30

Part

MONTHLY REPORT

DECLASSIFIED

Title: Purification of Ba¹⁴⁰ by Ion Exchange

By Authority Of:

E. J. Murphy 5-25-60

Jm

Work by: R. E. Blanco, A. H. Kibbey, G. C. Blalock, J. E. Farmer

For: M. T. Bray, Supervisor
Laboratory Records Dept.
ORNL

Secret Notebook No. 371

SUMMARY

Development of a Nuckel-Versene Process

Work is continuing on the development of the Nickel-Versene Process for the purification of Ba¹⁴⁰ by ion exchange where the maximum amount of barium plus strontium is 4 gms. (10,000 curies). The use of a resin column in the nickel form decreases greatly the size of resin column necessary to adsorb the barium. Since the nickel Versene complex is much stronger than the barium complex, the latter complex is broken as the feed passes through the column leaving the barium free to adsorb.

Two runs, in which no attempt was made to remove the sodium, yielded barium product of adequate purity with a yield in excess of 95%. Two subsequent runs, which included sodium removal by hydrochloric acid elution, showed large barium losses in the sodium waste. The use ~~of~~ of a higher resin column has apparently eliminated this loss, although final analytical results are not yet available.

The tentative full scale conditions and process steps are as follows:

Column: Dowex 50 resin, 60-100 mesh,
4"x39" bed(measured in H⁺ form)

Total process time: 19 hrs.

Flowrate: 0.7-1.2 ml/min/cm² column cross section

Process Steps:

- (1) Convert Resin to nickel form with 0.25 M sodium citrate, 0.25M nickel, at pH 2.3 (not included in process time)
- (2) Dissolve the barium-lead sulfate cake in Versene at pH 6.5 and pass through the resin bed followed by a water wash. The bulk of the nickel and lead pass out in the waste effluent while the barium and strontium are adsorbed.
- (3) Elute the strontium and other impurities in pH 6.3, 0.07M Versene.
- (4) Elute the sodium in dilute hydrochloric acid.
- (5) Elute the product in 6M nitric acid.

To: F. L. Steahly

Date: August 9, 1950

From: R. E. Blanco

Report Period: 5/10-8/10/50

Distribution:

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DECLASSIFIED

Problem No. TDSI-30

Part

Q U A R T E R L Y R E P O R T

FLS-422
Chemical Technology Division
Laboratory Section

By Authority Of:

E. J. Murphy 5-25-66

pmh

For: M. T. Gray, Supervisor
Laboratory Records Dept.
ORNL

Title: Purification of Ba¹⁴⁰ by Ion Exchange

Work by: R. E. Blanco, A. H. Kibbey, G. C. Blalock, J. E. Farmer

Secret Notebook No.

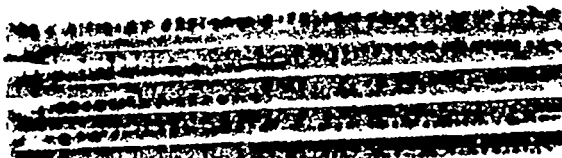
SUMMARY

I. Metathesis - Versene Process

The Metathesis - Versene Process has been chosen as the production process for purification of radio-barium. Demonstration runs, designed to determine the critical features of this process, showed that raising or lowering the amount of lead in the Versene feed solution by 20% did not materially effect the yield or purity of product. It was also found that there was no difficulty in meeting the iron specification for product purity when the resin was properly cleaned prior to use. An order has been placed with Dow Chemical Co. to supply C. P. resin free from iron and organic impurities.

II. Nickel - Versene Process

The Nickel - Versene Process has been developed to simplify the Ra La Process by replacing the metathesis and purification steps with a one-column



ion exchange process. This process has been designed to handle up to 4 grams total of barium and strontium (15,000 curies). The lead-barium sulfate cake is dissolved in Versene at pH ~~6.5~~ - 6.5 and passed through a resin column. The use of a resin column in the nickel form greatly decreases the size of column necessary to adsorb the barium. This effect is a result of the great difference in the Versene complex constants of the nickel and barium. As the feed passes through the column, the nickel is selectively eluted and complexed by the Versene, leaving the barium free to adsorb.

Several runs have shown barium yields in excess of 95%. The amounts of impurities present in the product have been slightly over tolerance, however. The process refinements in use on demonstration runs now in progress are expected to result in product of adequate purity.

The tentative full scale conditions and process steps are as follows:

Column: Dowex-50 resin, 60 - 100 mesh
4" x 45" bed (Measured in H⁺ form)

Total process time: 20 hours

Flow Rate: 0.7 - 1.2 ml/min/cm² column cross section

Process Steps:

- (1) Convert resin to nickel form with 0.25 M sodium citrate, 0.25M nickel, at pH 2.3 (not included in process time)
- (2) Dissolve the barium-lead sulfate cake in Versene at pH 6.5 and pass through the resin bed followed by a water wash. The bulk of the nickel and lead pass out in the waste effluent while the the barium and strontium are adsorbed.
- (3) Elute the strontium and other impurities in pH 5.5 0.07M Versene.
- (4) Elute the sodium in dilute hydrochloric acid.
- (5) Elute the product in 6M nitric acid.

III. Solubility Studies

Graphs have been prepared showing the solubility of barium strontium and lead sulfates in Versene as a function of pH, sulfate concentration and barium, strontium and lead concentration.

IV. Preparation of Pure Radio-Barium from MTR Assemblies

Preliminary efforts are being directed toward selective dissolution of the aluminum from the assemblies with a mixture of sodium hydroxide (free from carbonate) and sodium nitrate. Such a procedure would decrease the number of moles of material in process from approximately 164 to 1.

Two caustic leachings were performed on pile irradiated samples of uranium - aluminum alloy clad with aluminum. The results show that 99% of the total aluminum, corresponding to 96% of the alloy aluminum, was dissolved, while 4% of the uranium and 2% of the barium was found in the solution. Efforts in experiments now in progress are directed toward reducing the amount of uranium lost.